# EVALUATING OPTIONS FOR CHANGING GROUNDWATER MONITORING REQUIREMENTS FOR LANDFILLS TO REDUCE MERCURY USED BY LABORATORIES

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## Executive Summary

The State of Wisconsin requires aqueous environmental samples at solid waste landfills to be tested for chemical oxidation demand (COD). The typical COD analytical method generates toxic waste that includes mercury, chromium, and silver. The Wisconsin Department of Natural Resources (WDNR), in an effort to reduce mercury and other toxic metals waste, initiated this study to determine the effectiveness of COD monitoring, whether COD analyses can be replaced with an effective and less polluting alternative, or eliminated without sacrificing the ability to detect groundwater contamination from landfills.

The study was divided into three phases. Phase I determined the usefulness of COD for detecting groundwater contamination from landfills. Phase II determined if other required monitoring parameters would identify groundwater pollution if COD was not used. Landfills selected for study in Phases I and II had known contamination problems. Phase III compared of other non-required analyses or combination of analyses to determine if they could detect groundwater contamination and redox condition with less environmental impact than COD. Analyses selected for the side-by-side comparison with COD included: redox potential (Eh), manganese (Mn), iron (Fe), ammonium ($NH_4$), dissolved organic carbon (DOC), Hach Mn III COD, and dissolved oxygen (DO).

Based on the evaluation performed in Phases I and II, twenty-four landfills were selected as possible sites for field study. These sites included 14 municipal solid waste (MSW), 6 paper mill sludge, 1 demolition waste, 1 municipal solid waste combustor ash, 1 fly/bottom ash, and 1 foundry landfill. Landfill types represented by only one site were eliminated from Phase III field sampling for statistical purposes, leaving MSW and paper mill sludge landfills. Samples were collected in the spring and fall of 2000 at 12 municipal solid waste and 6 paper mill landfills. Sites selected for the study have at least one up-gradient and three downgradient groundwater monitoring wells. Phase III did not include leachate and lysimeter samples.

WDNR's Groundwater and Environmental Monitoring System (GEMS) database was used extensively for Phases I and II. Upgradient and downgradient wells were identified for each selected landfill. Box plots and time versus concentration graphs for parameters at up- and downgradient wells were used to determine groundwater contamination. Phase I found COD was useful in detecting landfill contamination in only 15 of 46 sites identified as having impacted groundwater. The COD method was apparently more useful in identifying contamination from paper mill and MSW combustor ash sites than from other landfill sites. COD alone was not an effective indicator of groundwater pollution. Phase II found required detection monitoring parameters other than COD were useful in identifying landfill contamination in 45 of 50 sites identified as having impacted groundwater. Parameters such as conductivity, alkalinity, hardness, iron, and VOCs were useful individually or in combination. These indicator parameters identified groundwater problems in 90% of the cases studied as compared to only 33% for COD.

Paper mill and MSW sites selected for the Phase III study represented a wide range of construction design, geologic environments, and degree of groundwater contamination. Statistical analyses included plotting paired data of individual parameters versus COD and DOC and applying the Pearson Correlation Coefficient to the plots. Data from a few heavily contaminated sites were eliminated from most statistical analysis because they skewed correlations and masked potentially more important relationships at the break-through level.

Phase III determined that DOC is an excellent replacement analyte for the mercury COD test. The DOC test does not use mercury or produce a toxic waste and is at least ten times more sensitive than the COD method. The greater sensitivity of this method may be significant in identifying early landfill leachate impacts on previously uncontaminated groundwater. DOC also correlates well with most other pollution indicators used in this study at both paper mill and MSW sites.

The Hach Mn III COD method had poor sensitivity and thus, investigators found it inadequate for early detection of contaminants to groundwater. The method may have some utility in monitoring sites heavily contaminated with organics or reduced metals. Eh, Mn, Fe, $NH_4$, and DO have adequate sensitivity as early indicators of groundwater contamination and correlate well with Hg COD and DOC under most conditions. The effectiveness of Eh and DO as pollution indicators is limited by naturally reduced groundwater conditions and by oxygen introduction during well purging. The accuracy of Eh results is also affected by electrode calibration and electrode poisoning. Mn and Fe effectiveness are limited by: naturally reduced groundwater, oxygen introduction during well purging, Fe oxidation and precipitation prior to filtering and preservation, and the lack of these elements in some aquifers. $NH_4$ is a good indicator parameter since it is not commonly found in natural groundwater, however, it is not clear how soon it shows up in contaminated monitoring wells. It is also oxidized quickly in most aquifers.

By design, this study was biased toward landfills with known contamination problems so conclusions about the COD's effectiveness as an indicator parameter reflect that bias. The results suggest that analytes other than COD could be useful as indicators of groundwater contamination from landfills. All alternative parameters tested are good indicators of pollution in some groundwater matrices. It is clear that no one analyte is an effective diagnostic tool under all conditions or at every landfill site. Multiple parameters are necessary to effectively monitor groundwater at all landfill sites. Although monitoring for Volatile Organic Compounds (VOCs) is not required for most landfill types, VOCs were important for identifying contamination at several landfills. The best combination of analytical tests could be site specific based on the type of waste and background water quality at each landfill.

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## Introduction

The Wisconsin Department of Natural Resources (WDNR) requires solid waste landfills to monitor groundwater and leachate to determine if the landfills are adversely affecting the environment. Required indicator parameters include chemical oxygen demand (COD). WDNR staff have questioned COD's utility as an indicator of leachate reaching groundwater. Traditional COD analyses use reagents containing chromium, mercury, and silver which can pose health hazards for laboratory personnel and generate hazardous wastes that can threaten human health and the environment. Mercury is of special concern because of its high volatility, mobility and ability to transform into more toxic forms once in the environment. Reducing or eliminating monitoring requirements for traditional COD analyses would benefit environmental quality by reducing the amount of mercury released to the environment.

This study was conducted in three phases. In Phase I, investigators evaluated results for COD, inorganic indicator parameters, and VOCs at selected landfills to determine which parameters successfully identified groundwater contamination. During Phase II, we evaluated the data from Phase I as a whole and grouped the landfills by type of waste disposed to determine whether other required monitoring parameters could be used to identify groundwater pollution independently of COD.

We used WDNR's Groundwater Environmental Monitoring System database (GEMS) to review groundwater and leachate sampling results. Data in GEMS includes landfill compliance monitoring data, well construction information, well gradient location, monitoring schedules, and groundwater standards for the compounds being sampled at each site. GEMS can generate reports of groundwater standard exceedances and statistical analyses, routinely used by WDNR Waste Management program hydrogeologists, waste management specialists, and other staff.

Phase III evaluated the effectiveness of other analytes or combination of analytes in indentifying groundwater contamination and redox conditions. Investigators selected redox potential (Eh), dissolved manganese (Mn), dissolved iron (Fe), ammonia (NH4), dissolved organic carbon (DOC), dissolved oxygen (DO), and HACH Mn III COD for side by side comparison with COD. The twenty-four landfills selected as possible sites for groundwater sampling were classified by waste types: (14) municipal solid waste, (6) paper mill sludge, (1) demolition, (1) municipal solid waste combustor residue, (1) fly/bottom ash, and (1) foundry waste. Sites selected for the study had at least one up-gradient and three down-gradient/side gradient monitoring wells. Statistical analysis by landfill type was limited to municipal solid waste and paper mill sludge landfills.

WDNR had primary responsibility for Phases I and II of the study and the UW-Stevens Point Environmental Task Force Program had primary responsibility for Phase III, however, collaboration occurred during all phases of the study.

## Objectives

The objectives of this project were to:

1) evaluate the effectiveness of using COD to identify groundwater contamination at solid waste landfills accepting various categories of waste and
2) evaluate alternative methods or analyses to potentially replace COD at sites with waste types where COD is effective.

## Literature Review

## Mercury Toxicity

The results of research conducted since the 1950's show mercury emissions to the environment represent a serious threat to human health. Early studies demonstrate that fish and other wildlife accumulate toxicologically significant mercury levels when directly exposed to mercury-containing emissions from human-related activities. Health concerns arise when humans consume fish and wildlife from these ecosystems.

Investigations initiated in the late 1980's in the northern-tier states of the U.S., Canada, and Nordic countries found that fish, mainly from nutrient-poor lakes and often in very remote areas, have high levels of mercury (Manno, 1995; Lucotte, 1995; Sang, 1995). More recent fish sampling surveys in other regions of the U.S. have shown widespread mercury contamination in streams, wetlands, reservoirs, and lakes. To date, 33 states have issued fish consumption advisories because of mercury contamination. Surveys by WDNR show that one in three of the 3,000 Wisconsin lakes that have been tested received a mercury advisory. Twenty to 30 additional lakes are added to that warning list each year (Esposito, 1998).

Once in an aquatic environment, mercury is transformed by bacteria to methylmercury, a highly toxic form (Krabbenhoft; 1997). Methyl-mercury bio-accumulates in the food chain and there is strong evidence that bio-magnification occurs.

## Mercury Wastes from Current COD Methodology

One of the WDNR Secretary's objectives is to reduce emissions of mercury to the environment. In WDNR's search for ways to eliminate mercury, staff identified that laboratories routinely use mercury and other toxic metals as reagents. These toxic metals end up in the laboratory's waste stream. The emphasis on mercury reduction has led WDNR staff to question whether COD is a valuable indicator of groundwater contamination and whether acceptable alternatives are available. Chemical Oxygen Demand or COD merited closer attention because of the large number of analyses required and because COD analyses generate mercury wastes. Active landfills are required to analyze environmental samples semi-annually for a suite of indicator parameters, including COD, while most closed facilities perform quarterly or semi-annual COD analyses.

WDNR is concerned that:

- Data reviewers rely on COD results much less frequently than results from other required indicator parameters when evaluating contamination at landfills;
- COD may be appropriate for some waste types such as MSW but not for others such as utility ash and foundry waste, yet present rules require that COD be tested in groundwater at all landfills regardless of waste type accepted;
- Data reviewers may assume erroneously that COD is an effective indicator of VOC or other organic contamination, and
- Existing COD data may be skewed because of sampling or analytical error.

## What is COD?

COD is a nonspecific analytical test that determines the amount of oxygen [in mg/l] required to oxidize both organic and oxidizable inorganic compounds in a sample. The traditional COD test method uses a reagent containing potassium dichromate (oxidant), silver sulfate (catalyst), and mercuric sulfate [$HgSO_4$], in a 50% sulfuric acid medium (Boyles, 1997). The waste produced by the test method contains silver, chromium and mercury; heavy metals regulated under federal hazardous waste regulations. COD indirectly measures inorganic parameters subject to oxidation such as $Fe^{-2}$, $S^{-2}$, N, and Mn. It also measures oxygen demand from organic compounds [$C_aH_bO_c$] found in leachates such as organic acids (Evanson, 1987). Currently, COD is the only indicator parameter used to detect organic material in leachates and groundwater and indicate redox conditions present in the groundwater. As reducing conditions increase, the COD values increase.

Advantages

- The test can be performed in 2 to 3 hours.
- Toxic materials do not interfere with the test.
- COD can provide some clues as to whether there are oxidizing or reducing conditions in the subsurface.

Disadvantages

- Groundwater results tend to be quite variable, making it more difficult to draw conclusions from the data.
- Organics in the air can bias sample results, particularly at concentrations below 20 mg/L.
- The sensitivity of the low level COD test may affect the reliability of results for relatively clean groundwater. (The working range for low level COD is approximately 5 - 50 mg/L.)
- All oxidizable material (such as iron) will contribute to COD.
- The precision of the test varies with a 5-10% standard deviation, although the variation can be greater in samples with high levels of suspended solids.
- High levels of chloride ($Cl^-$) can interfere with the test.
- Some types of organic compounds are oxidized incompletely.
- This test is non-specific since it cannot identify what is causing the demand.
- Some understanding of zonation that occurs in aquifers around contaminated landfills is necessary to interpret the results.
- The test generates toxic waste.

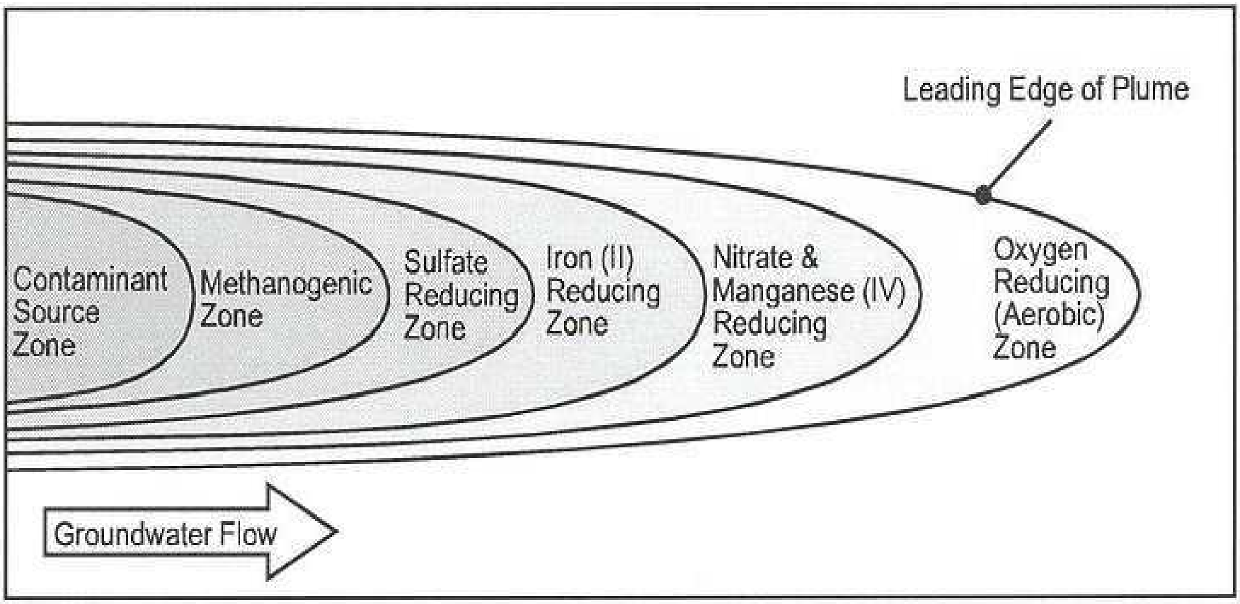
Based on data from 1996 and 1997, WDNR records show that, on average, landfill operators submitted about 14,500 COD results for groundwater, leachate and lysimeter fluid samples per year. According to one chemist contacted (Parker, 1998), when a 10 ml sample is used, the test produces between ½ to 1 gallon of waste for a group of 20 samples with its associated quality control. If we estimate the annual volume of waste generated using current COD protocols with a reduced sample size of 2 mL, we calculate a conservative estimate of 45,000 gallons of waste per year generated from testing environmental samples from Wisconsin landfills for COD.

## Alternatives to Traditional COD Analysis

In evaluating the alternatives to measuring COD, we needed to understand what the test measures, the processes it monitors, and whether the test measures effectively the conditions of concern. COD directly measures organic material in a sample and is an indirect measurement of reducing conditions. In leachate monitoring, COD measures oxidizable materials originating from waste or waste release at the landfill. In groundwater, COD serves as an indirect measure of contamination by indicating if reducing conditions are present. As reducing conditions increase, COD increases. Because COD is the only required indicator parameter that tests for organic material and redox conditions present in the groundwater, investigators considered cautiously the prudence of eliminating COD from the list of routine groundwater monitoring requirements. In seeking alternative tests that generate less hazardous waste, investigators focused on the geochemistry associated with reducing conditions associated with groundwater contamination.

Geochemical zonation around leaking landfills that results in reducing conditions was identified by Baedecker and Back (1979). As leachate seeps from the landfill into the underlying soil, decomposition reactions consume available free oxygen and the plume becomes more reducing (i.e., the redox potential decreases). Under these conditions, manganese and iron hydroxides in the soil dissolve and manganese ($Mn^{2+}$) and iron ($Fe^{2+}$) become mobile. Continued degradation of organic compounds causes greater lowering of redox levels until ammonia ($NH_4^+$) is the dominant N species. Sulfate is also reduced: hydrogen sulfide ($H_2S$) is the dominant reduced S species at pH of less than about 7 (the usual situation), while $HS^-$ is dominant at slightly higher pH values. The reduction of sulfuric acid ($SO_4^{2-}$) uses the last source of oxygen, other than organic material itself, and organic compounds then degrade anaerobically by processes of fermentation to form carbon dioxide ($CO_2$), ammonia ($NH_4^+$), and methane ($CH_4$). This highly reduced zone is typical of the subsoil closest to the landfill. As uncontaminated, oxygenated groundwater mixes with the leachate plume further from the landfill, redox levels increase and a series of zones are established in which the dominant redox-sensitive species change progressively in reverse of the above series of reduction reactions. Methane and $CO_2$ dominate the zone closest to the landfill, while $H_2S$, $NH^{4+}$, $Fe^{2+}$, and $Mn^{2+}$, respectively, dominate with increasing distance from the leachate source until free dissolved oxygen is present in the groundwater and the system is aerobic once again. (Figure 1).

FIGURE 1. SCHEMATIC SHOWING GROUNDWATER ZONATION AROUND A LANDFILL.




Source: Modified from Anderson, R.T. and D.R. Lovley 1997

Based on the processes described above, investigators saw three options for substitution: find alternate measurements of organic material that correlate well with the presence of contamination, find another measurement that indicates reducing conditions, or identify alternate methodology for measuring COD that reduces the amount of hazardous waste generated. Investigators identified three tests that met these needs: dissolved organic carbon, redox potential (Eh) and Hach's MnIII COD method.

Dissolved organic carbon [DOC] may be an attractive substitute for COD in directly measuring contamination from landfills. Organic leachates originating from municipal solid waste (MSW), papermill sludges, and, to a lesser extent, foundry wastes should contain substantial amounts of carbon. In theory, the processes described by Baedecker and Back dominate when leachate is released. The organic carbon, in the form of weak organic acids, enters the groundwater where it oxidizes to form $HCO_3^-$. As conditions change from oxidizing to reducing, the carbon changes to $CO_3$, $CO_2$, and eventually C.

Investigators saw redox potential or Eh as a viable option for more directly measuring reducing conditions. In the last several years, a burgeoning interest in biodegradation and natural attenuation of organic compounds has led to the development and use of field Eh meters. As a result, Eh has become a relatively common and affordable field measurement. However, cost may be an issue at some sites and the accuracy of the determination may be affected by the depth to the sample.

The Hach Company has developed a new methodology (Hach, 1997a) called the Manganese III [MnIII] Method for COD, which takes about 90 minutes to perform. The method uses trivalent manganese as an oxidant that changes color when it reacts with organic matter. The results are measured colorimetrically and the color change is inversely proportional to the amount of COD in the sample. Known interferences for this method are chloride and ammonia when chloride is present. The chloride can be removed by sample pretreatment with a Chloride Removal Cartridge manufactured by Hach. Hach states that the MnIII method theoretically oxidizes about 70 – 80% of the theoretical oxygen demand value of organic compounds compared to 95 to 100% for the dichromate method (Hach, 1997b). The MnIII procedure does not generate toxic metal-bearing wastes like the EPA method does; however, it is not EPA-approved.

Investigators included manganese, iron, ammonia, and dissolved oxygen in the Phase 3 evaluation because these parameters are part of the geochemistry described by Baedecker and Back for zonation and reducing conditions. These fairly inexpensive parameters can be determined by multiple procedures readily available in environmental laboratories.

## Phase I and II

We expanded on a preliminary study (Hegeman, 1998) performed on landfills in the northeastern part of the state which found COD to be more valuable at certain types of landfills than others. Phase I was designed to determine whether results for COD and inorganic indicator parameters effectively identified groundwater contamination from the landfills. A parameter was considered effective for detecting groundwater contamination if concentrations in the downgradient wells were elevated in comparison with upgradient results or if the data indicated trends that match trends for other parameters and correlated to the site's history. In Phase II, we evaluated how effective COD has been overall in identifying landfill contamination of groundwater. Investigators considered COD effectiveness for the entire data set and then grouped by different waste types accepted at the landfills. Our methods included selecting candidate sites for study, reviewing site history, statistical analysis of available monitoring data, an evaluation of leachate COD results, preparing data assessment summaries for each site, and compiling the effectiveness determinations into tables for each type of landfill. We assumed that wells were statistically located to best detect contamination from the landfills, facilities used proper sample collection and analytical techniques and data were valid

## Preliminary Site Selection

In selecting sites, investigators sought sites with known contaminant plumes, adequate monitoring well placement, and sufficient monitoring data to identify trends. Older, unlined sites were considered as the most likely candidates to meet the selection criteria. After considering the total number of regulated sites, the amount of data in WDNR databases, and the time required to screen that data to identify candidate sites for study, investigators opted to query WDNR staff familiar with the landfills for their recommendations. We asked staff to identify older sites with known or suspected groundwater contamination at some time in their history for use in this study. Most of the 50 sites recommended had old, unlined phases. We considered VOC concentrations in excess of the Chapter NR 140, Wisconsin Administrative Code (NR 140) preventative action limits (PALs) detected in groundwater at some of the sites to be concrete evidence that the landfill was leaking. PALs are values set below groundwater standards that, when exceeded, allow facilities to take action prior to reaching the groundwater standards.

## Site History

The principle investigator in Phase I reviewed WDNR files to assure that background or upgradient wells could be identified and to compile a brief site history. Identifying background or upgradient wells was crucial for comparing those wells to downgradient wells to identify contamination originating from the landfill. If no gradients were specified in the Groundwater and Environmental Monitoring System (GEMS) database, the investigator contacted the staff person who recommended the site or consulted the files for maps, plan sheets, reports, or remedial action documentation to determine the gradient. The site history provided a basic understanding of the geology and hydrogeology to help explain natural variations in the data. Additionally, knowing operation dates and significant events such as cap placement or remedial action events helped explain spikes, dips, or trends in the data. For some sites, the available data was limited to the minimum tests required by Administrative Code. At other sites, additional monitoring had been performed.

Section NR 507.30, Wisconsin Administrative Code, outlines the groundwater monitoring requirements at landfills based on waste type accepted for disposal. Table 1 identifies parameters evaluated in this study for municipal solid waste (MSW), MSW combustor residue, paper mill sludge, fly ash or bottom ash, foundry waste, and demolition waste landfills. Indicator parameters, as defined in s. NR 140.20, are in Italics, while the NR 140 public health and welfare parameters are in regular type.

**Table 1 – Groundwater Monitoring Parameters Based on Waste Type**

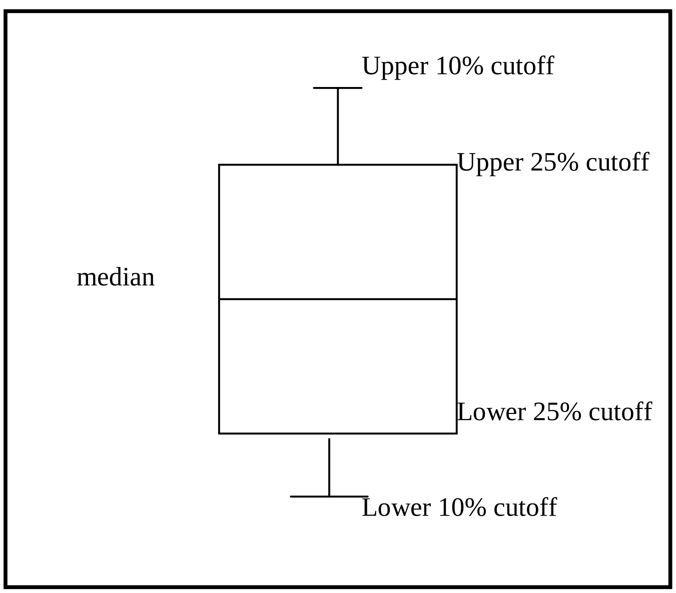
| Parameters | Municipal Solid Waste (MSW) | MSW Combustor Residue | Paper Mill Sludge | Fly or Bottom Ash | Foundry Waste | Demolition Waste |
|---|---|---|---|---|---|---|
| *Alkalinity* | X | X | X | X | X | X |
| *Chloride* | X | X | X | X | | X |
| *COD* | X | X | X | X | X | X |
| *Field Conductivity* | X | X | X | X | X | X |
| *Field pH* | X | X | X | X | X | X |
| *Hardness* | X | X | X | X | X | X |
| *Ammonia Nitrogen* | | | X | | | |
| *Boron* | | X | | X | | |
| Cadmium | | X | | | | |
| Fluoride | | | | | X | |
| Lead | | X | | | | |
| Nitrate + Nitrite | | | X | | | |
| Selenium | | X | | | | |
| Sodium | | | | | X | |
| Sulfate | | X | X | X | | X |
| VOC Scan | X | | | | | |

## Statistical Analysis of Monitoring Data

The monitoring data used in this study are stored in the GEMS database, first developed at WDNR in 1979 to manage groundwater data from samples collected at landfill monitoring wells. GEMS is capable of providing statistical analyses of data. We also used GEMS to develop box plots and time versus concentration graphs used for this study. Box plots and time versus concentration graphs are nonparametric visual statistical methods recommended by Dr. Kenneth Potter (Fisher and Potter, 1989) for statistical analysis of water quality data, and other data that do not fit normal distribution patterns. Although investigators considered additional statistical analyses, they did not add to the understanding of the data so they were discarded.

Using the list of recommended contaminated sites, box plots were created for each parameter required to be analyzed for a particular type of landfill (Table 1). Two sets of box plots were printed for each site: monitoring wells and leachate collection systems or lysimeters. Box plots organize data visually to show differences in the concentration of water quality parameters at different monitoring point locations. A horizontal line inside the box (Figure 2) indicates the median (middle value) of the distributed data in the box plot. The upper and lower bounds of the box represent the upper and lower 25% cutoff points for the data. The area between the upper and lower 25% is the interquartile range (IQR) or middle 50% of the data. The median and the interquartile range (IQR) are analogous to the more common mean and standard deviation of a set of data (Fisher and Potter, 1989). The median is a measure of "central tendency" or "location", whereas the standard deviation and the IQR are measures of "variability". The vertical lines with bars at the end that extend above and below the box show the upper and lower 10% cutoff points for the data. Data outside of the 10% cutoff points are considered outliers. An elongated box with a large IQR indicates a wide range of data and is often characteristic of a contaminated well. A more squat box with a small IQR indicates that most of the data are close to the median value and typically is characteristic of an uncontaminated well. Box plots with medians and IQRs that are above those for the majority of wells at a site also are considered characteristic of a contaminated well.

FIGURE 2. DIAGRAM OF A BOX PLOT WITH DATA RANGES INDICATED



We focused much of our attention on the monitoring wells and developed box plots for all the groundwater quality data for each inorganic parameter sampled at a given landfill. We developed box plots for each landfill using both concentration values and non-parametric values. The boxplots using the non-parametric scale establish zero NP (non-parametric) value as the site median for the parameter being displayed and adjust the concentration values for the parameter at each well to non-parametric values. Appendix 3 includes both types of box plots for conductivity at three landfills.

For the box plots using concentration values we used the following criteria to choose monitoring wells that may be contaminated:

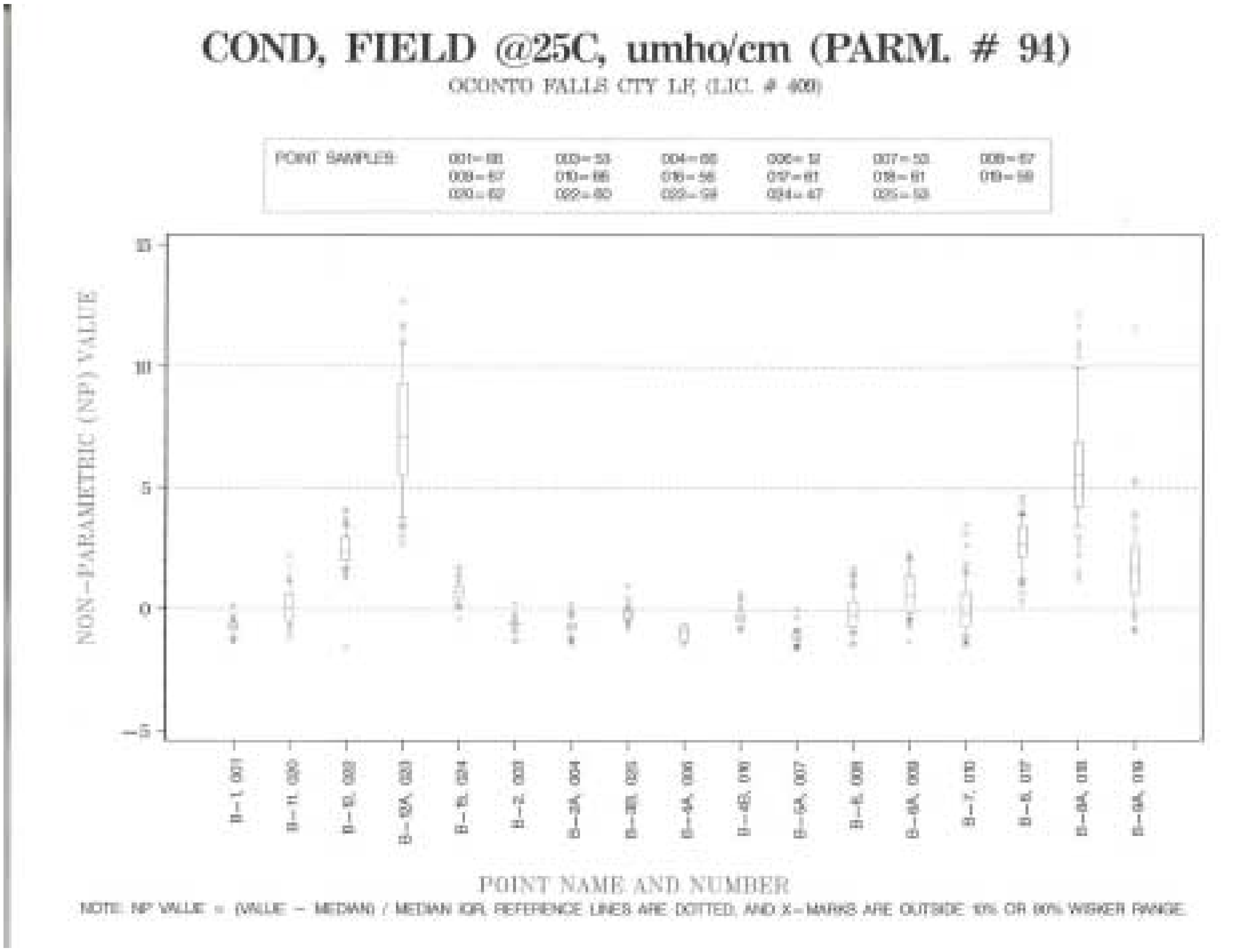
- large IQRs and high medians
- for a given parameter, elevated median and IQR above the medians and IQRs of other wells at a site or
- elevated median and IQR at or above the preventive action limit for the parameter.

For the box plots using non-parametric values, based on advice from Ken Potter and our staff's experience, we considered it likely that wells were contaminated if the median or IQR was at or above the non-parametric value of 5

For example, a box plot of specific conductance (conductivity) data from the City of Oconto Falls Landfill is shown in Figure 3. From this box plot, investigators selected downgradient wells B-12A and B-8A for the time versus concentration graph because the median and IQR for these wells is clearly over the NP value of 5. Additional wells B-8, B-9A and B-12, whose data were less clear because they were elevated, but not above the NP value of 5, were also added to the graph. The downgradient wells data were compared with the data in upgradient well B-1.

While the box plots helped determine if there was an overall impact in downgradient wells, time versus concentration graphs allowed us to evaluate trends over time. GEMS limits graphing of time versus concentration for a specific parameter to six wells, therefore, after running box plots for each site, we selected four or five wells that appeared to be contaminated and one or two upgradient, unaffected wells, and created time vs. concentration plots for each indicator parameter. Where a PAL had been calculated for a parameter, we included it on the graphs as a reference level to help evaluate the degree of contamination present. Some of the trends observed in the time versus concentration graphs increased with time, as expected. Others decreased, possibly indicating that remediation efforts, or partial or total closure of the landfill had been effective. More complicated trends required a brief evaluation of the site's history to explain the data. VOC summary reports were run also for wells with parameters exceeding their PALs.

FIGURE 3: SAMPLE NON-PARAMETRIC BOX PLOT OF CONDUCTIVITY DATA FROM CITY OF OCONTO FALLS LANDFILL




## Leachate COD Evaluation

Twenty-one of the 50 sites reviewed had leachate data available in GEMS for review. Leachate strength is a function of many factors, not limited to waste type, age, moisture control and phase of decomposition. Investigators evaluated COD results to determine whether it was the first or only sign of groundwater contamination or whether COD was elevated in groundwater but not in leachate. We found that COD results for leachate were not the first sign of contamination for any of the landfills. At many sites, the leachate data was not particularly useful because the leachate collection systems were installed in cells constructed later in the site's life, after results for groundwater indicator parameters indicated that contamination was present.

## Summarizing the Data

The investigator prepared different summary sheets for each landfill type to account for the variations in monitoring requirements. For each parameter monitored, the summary sheet identified how results compared to background concentration, any trends in the results, and whether similar trends were evident in leachate data. Many sites monitored extra parameters that were not generally required for that type of landfill; however, with the exception of VOCs, the additional data were not used in our assessment because their use was contrary to the purpose of this study. From these summary sheets, the investigator decided whether COD was an effective indicator parameter for each site. The VOC summaries used in this assessment were limited to those compounds present in excess of their PALs.

Ideally, investigators would make clear decisions about whether a certain parameter effectively identifies contamination. Either it does or it doesn't. In reality, the data may be less than clear. At times, results for COD or inorganic indicator parameters may show slight but unconvincing impacts or trends. VOC detections may be sporadic or the patterns in the well network may be confusing. Although site histories were helpful in explaining some fluctuations in the data, other fluctuations could not be explained. In these circumstances, investigators assessed the parameter as "Somewhat effective". Summary sheets for seven landfills can be found in Appendix 2.

## Phase I Results

The COD effectiveness assessments fell into four groups.

- COD Effective - 15 landfills
- COD Ineffective - 25 landfills
- COD Somewhat Effective - 5 landfills
- No COD Results Available - 5 landfills

Investigators did not plan for sites that had no COD data, but, by the time investigators discovered the problem, most of the site information had been assessed. Investigators chose to leave them in the study because we felt their assessments raised interesting questions. Four of the sites with no COD data were fly or bottom ash sites and one was a MSW site.

COD was effective at 30% of the landfills and ineffective at 50 - 60% of the landfills, depending on whether investigators assess COD as ineffective or unnecessary at landfills for which no COD results were available. At landfills for which the COD results were somewhat effective, investigators needed to consider whether the inorganic parameters or VOCs were effective to understand the importance of the COD data. Case studies put the COD effectiveness determination in context with the landfill operations and monitoring history, inorganic indicator parameter effectiveness, and VOC effectiveness and provided a foundation for investigators to determine COD's value as an indicator parameter.

## COD Effectiveness in Relation to Other Indicator Parameters

Table 2 shows the possible effectiveness assessment groups and the number of landfills in each group. We placed a value on COD results in each category based on how effective the inorganic parameters were in identifying contamination. When the inorganic parameters were assessed as *Somewhat Effective*, investigators decided that COD data was potentially necessary to add weight to the evidence that the landfill was causing contamination.

**Table 2. Indicator Parameter Effectiveness and Number of Landfills in Each Category**

| COD | Inorganic Parameters | Number of Landfills | COD Value |
|---|---|---|---|
| E | E | 14 | Not Useful |
| E | S | **0** | **Useful** |
| E | I | **1** | **Useful** |
| S | E | 3 | Not Useful |
| S | S | **2** | **Potentially Useful** |
| S | I | **0** | **Potentially Useful** |
| I | E | 24 | Not Useful |
| I | S | 1 | Not Useful |
| I | I | 0 | Not Useful |
| NA | E | 4 | Not Useful |
| NA | S | **0** | **Potentially Useful** |
| NA | I | **1** | **Potentially Useful** |

E = Effective S = Somewhat Effective I = Ineffective NA = Not Available

Most of the landfills (76%) fell into the *COD Effective/ Other Parameters Effective* (28%) or *COD Not Effective / Other Parameters Effective* (48%) categories and both categories contained each type of landfill studied. VOC data typically supported the inorganic parameters' effectiveness. At 14 of the 15 sites in which COD was effective, other indicator parameters were also considered effective in detecting the groundwater contamination. In assessments of *COD Not Effective / Other Parameters Effective*, if VOCs were even slightly helpful, the contamination would be detected.

Only 3 landfills fell into an *Inorganic Parameters Somewhat Effective* assessment. At the two landfills in the *COD* Somewhat *Effective/Inorganic Indicators Somewhat Effective* assessment group, VOC data clearly showed contamination. Investigators noted that for one of the sites, a Paper Mill Sludge landfill, VOC is not a required monitoring parameter. For the remaining landfill in this group, a MSW, COD was ineffective; however, VOC data indicated contamination.

## Case Studies

Case studies illustrate the how investigators rated the effectiveness determinations and classified sites. Three case studies are presented here, representing the categories in which most landfills were placed: *COD Effective, COD Ineffective, and COD Somewhat Effective*. Additional case studies are included in Appendix 1. The primary question investigators posed in reviewing each site was "Is COD data really necessary here?" Case studies include box plots for various parameters, time versus concentration graphs for selected wells, and a narrative of key factors used to determine the value of the COD results. On the graphs, a thick line with no symbol identifies upgradient wells used to establish background groundwater quality.

### *City of New Richmond Landfill*

The City of New Richmond Landfill, a municipal solid waste (MSW) landfill that accepted waste from 1970-1976, was officially closed in December 1977. The landfill is an unlined site with sandy soils overlying sandstone bedrock. Regulators suspect that zinc cyanide was disposed here. A report written in 1976 recommended that the landfill be abandoned and that no groundwater monitoring be required. Ironically, monitoring began in 1982 to determine whether the landfill could be expanded. The landfill was not expanded and monitoring of the closed landfill has continued to the present.

Of the 50 landfills evaluated, the City of New Richmond had the clearest increasing trend for COD. Time versus concentration graphs for the required indicator parameters are presented in Figures 3A-F. Well #6 represents background groundwater quality. Well #1, Well #2, and Well #3 are downgradient from the landfill.

FIGURE 3A. ALKALINITY CONCENTRATIONS CITY OF NEW RICHMOND LANDFILL MONITORING WELLS.

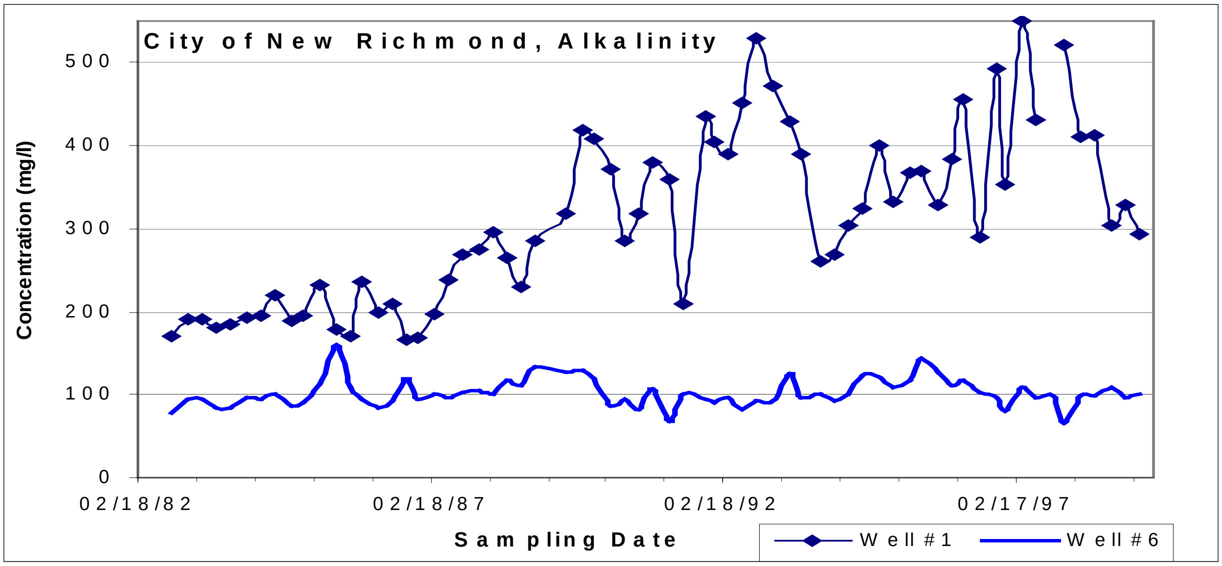



FIGURE 3B. CONDUCTIVITY IN CITY OF NEW RICHMOND LANDFILL MONITORING WELLS.

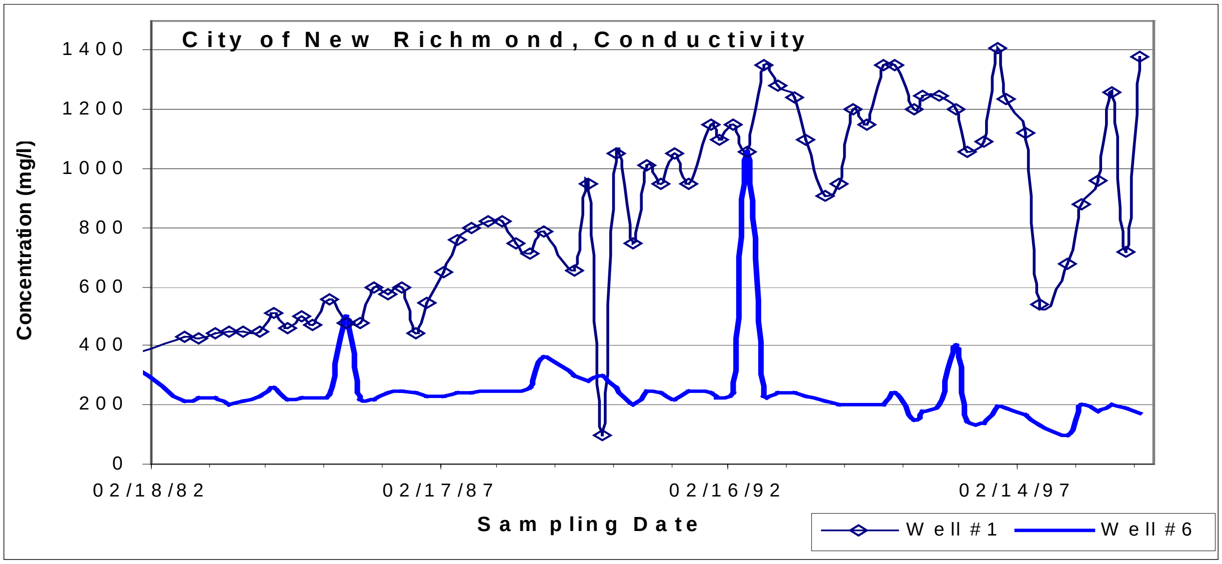


FIGURE 3C. COD CONCENTRATIONS IN CITY OF NEW RICHMOND LANDFILL MONITORING WELLS.

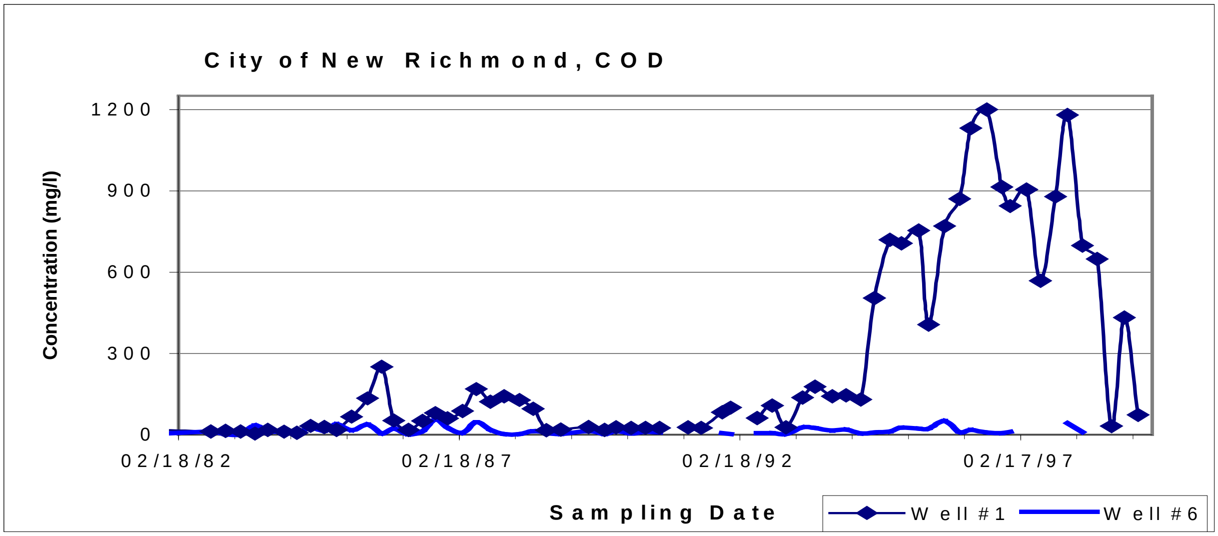



FIGURE 3D. CHLORIDE CONCENTRATIONS IN CITY OF NEW RICHMOND LANDFILL MONITORING

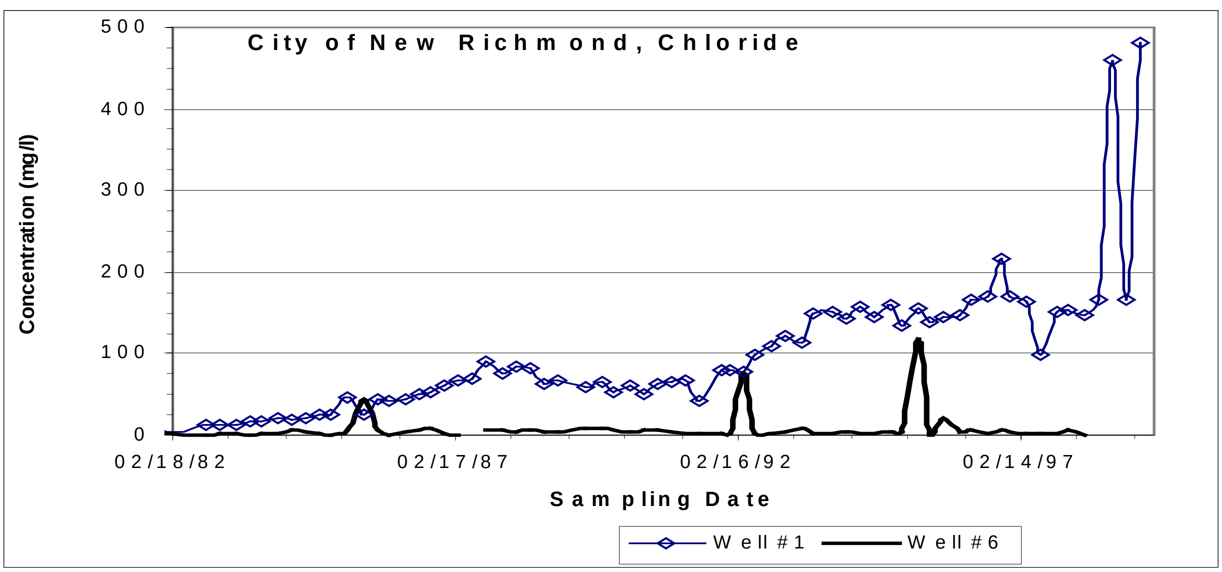
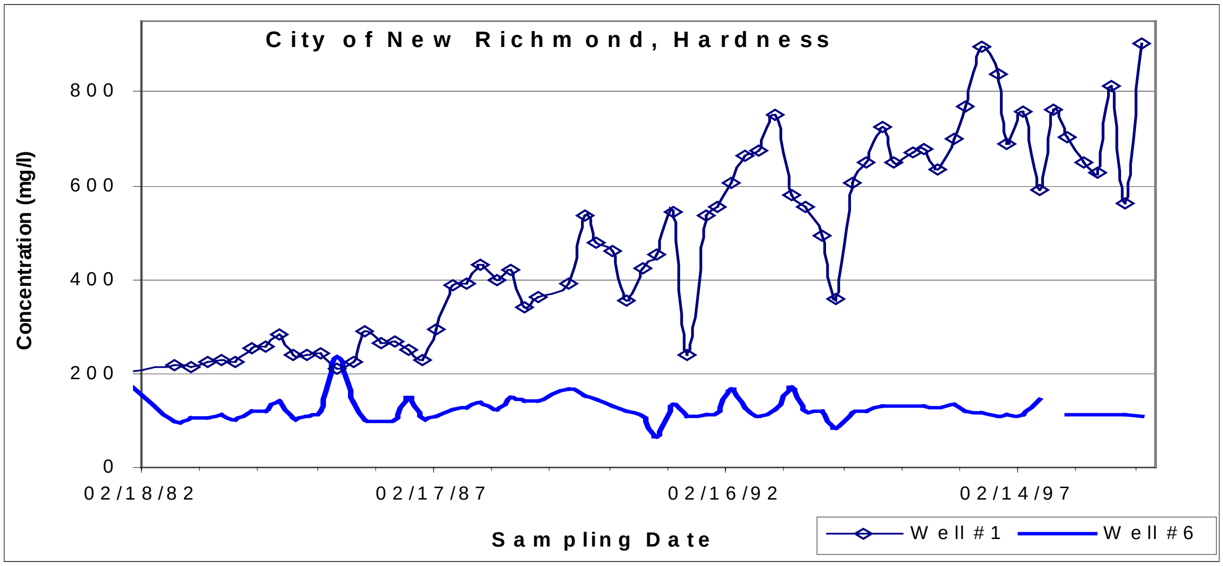


FIGURE 3E. HARDNESS CONCENTRATIONS IN CITY OF NEW RICHMOND LANDFILL MONITORING WELLS.




Investigators assessed the City of New Richmond as COD Effective, Other Parameters Effective. COD data for Well #1 shows a clear increase in contamination; however, the trend is not as clear in the other well (Figure 3C). Other parameters do a better job of detecting contamination for a majority of the wells. The time vs. concentration plot for alkalinity in Figure 3A shows that concentrations in downgradient well #1 are increasing with time. The difference between the downgradient well #1 and background well #6 are also very clear. Conductivity, (Figure 3B) and hardness (Figure 3E) show similar trends. For chloride (Figure 3D), concentrations exceed the 250 mg/l enforcement standard at times. The assessments from the graphs were summarized on the summary sheet for MSW landfills to help identify common themes for this type of landfill.

### *Marathon County Landfill*

The Marathon County Landfill operated from 1980-1993 and is clay lined. R-10 and R-11A are upgradient wells that were used to establish background groundwater quality. The facility or a WDNR staff member calculated Preventative Action Limits (PALs) for these two wells.

FIGURE 4A. ALKALINITY CONCENTRATIONS IN MARATHON COUNTY LANDFILL MONITORING WELLS

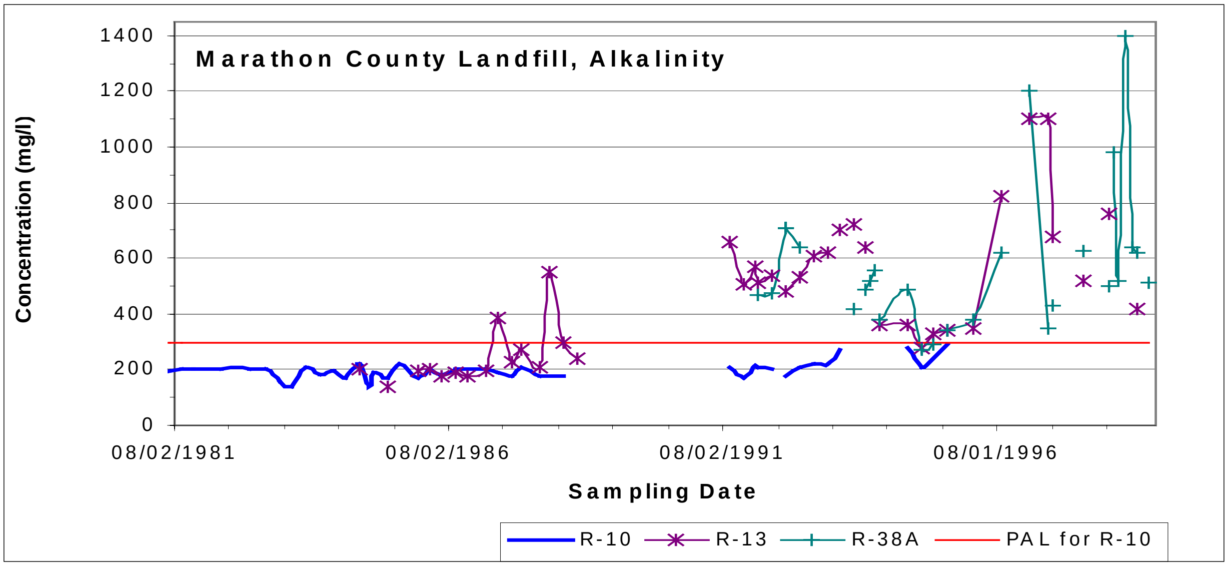



FIGURE 4B. COD CONCENTRATIONS IN MARATHON COUNTY LANDFILL MONITORING WELLS

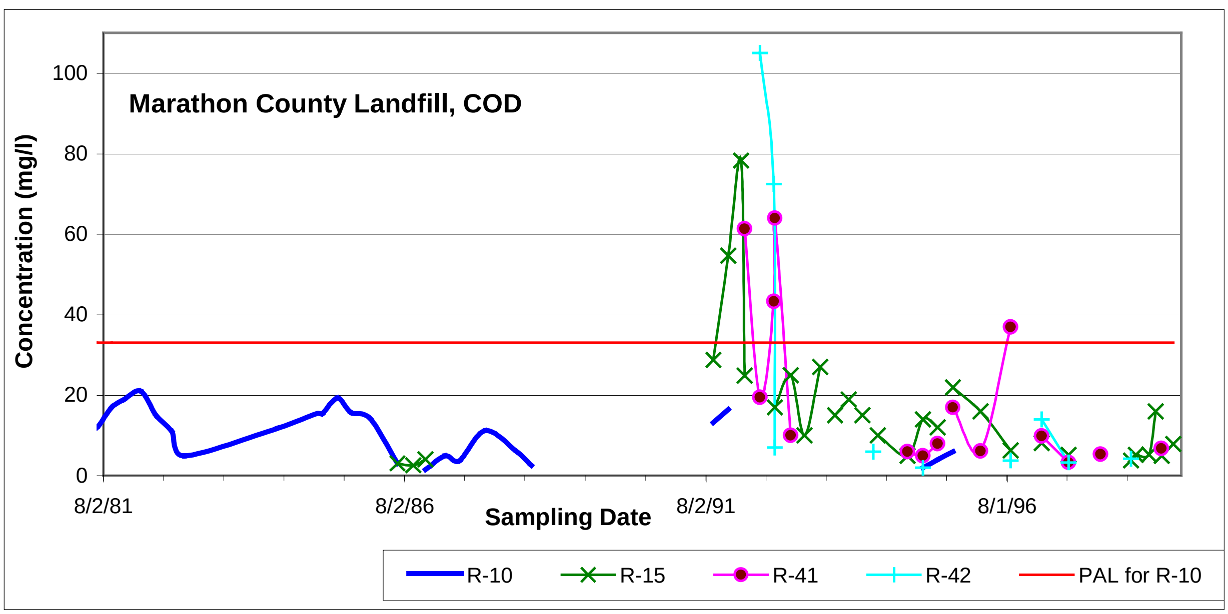


FIGURE 4C. CONDUCTIVITY OF MARATHON COUNTY LANDFILL MONITORING WELL SAMPLES.

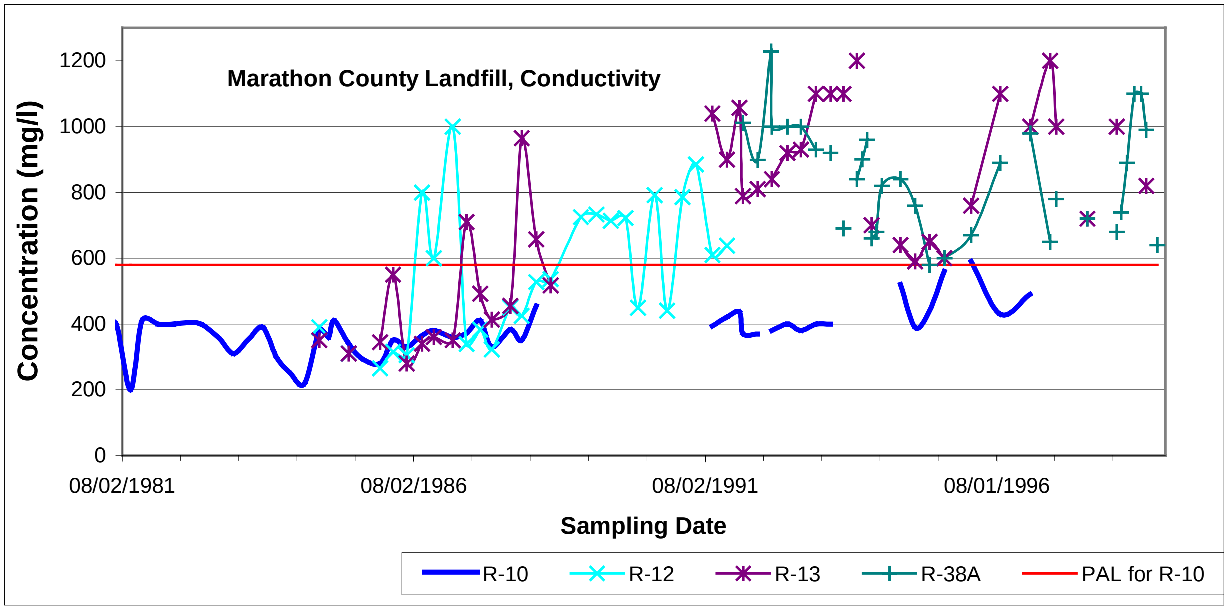
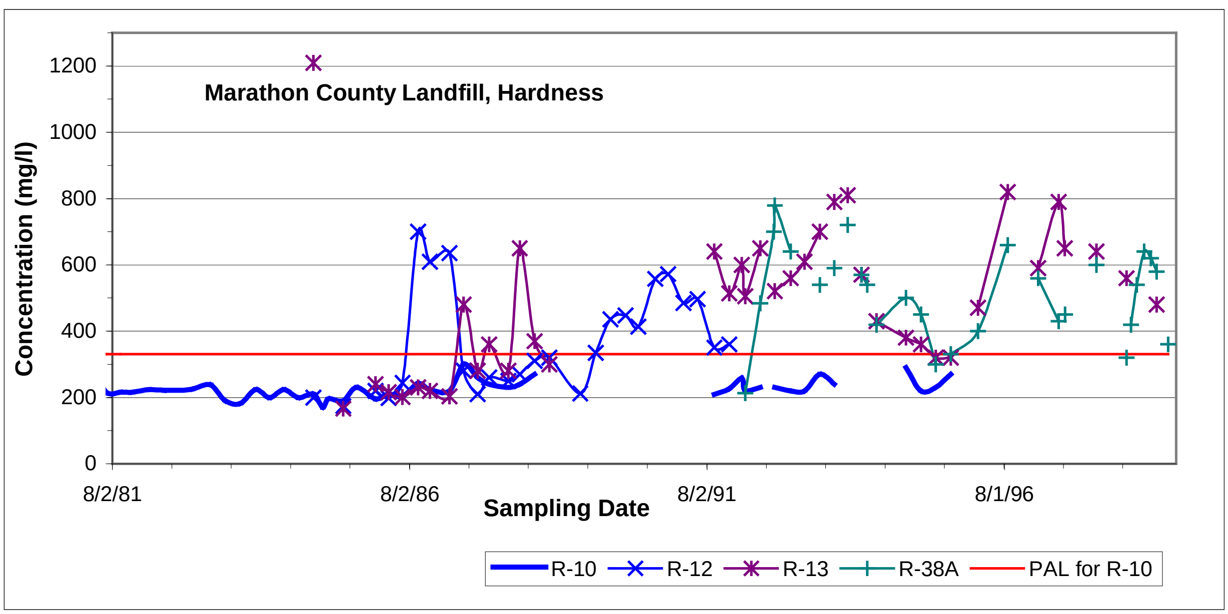



FIGURE 4D. HARDNESS CONCENTRATIONS IN MARATHON COUNTY LANDFILL MONITORING WELLS




Investigators assessed Marathon County Landfill as COD Ineffective, Other Parameters Effective. Alkalinity (Figure 4a), conductivity (Figure 4c), and hardness (Figure 4d) all show increasing trends with time. Also, a clear impact in downgradient wells is seen when compared to upgradient well R-10. COD data (Figure 4b) show enough variation that no overall impacts or a decreasing trend. From the graphs, it is clear that COD was not very useful in detecting contamination problems while other parameters were clearly showing the problems. Additionally, extensive VOC PAL/ACL exceedances were recorded.

### *City of Madison - Sycamore Landfill*

The City of Madison - Sycamore Landfill is an example of a site where groundwater monitoring indicator parameter data are confusing. On the surface, the data were somewhat useful because overall impacts were seen between upgradient and downgradient wells for most of the parameters. There were sporadic trends over time so the data did not provide clear evidence of contamination. Without VOC data, the contamination might have been difficult to detect. The GEMS VOC summary report shows many PAL exceedances.

For this site, it is important to understand the history and geology. There are differences in geology between upgradient and downgradient wells and also changes in well construction. Wells were sampled in the 1970s and '80s. Unfortunately, the older data may not be comparable to that generated in the last 5 - 10 years.

For this site, MW-12A, MW-19A, and MW-19B are upgradient wells used to establish the background groundwater quality.

FIGURE 5A. ALKALINITY CONCENTRATIONS IN MADISON SYCAMORE LANDFILL MONITORING WELLS

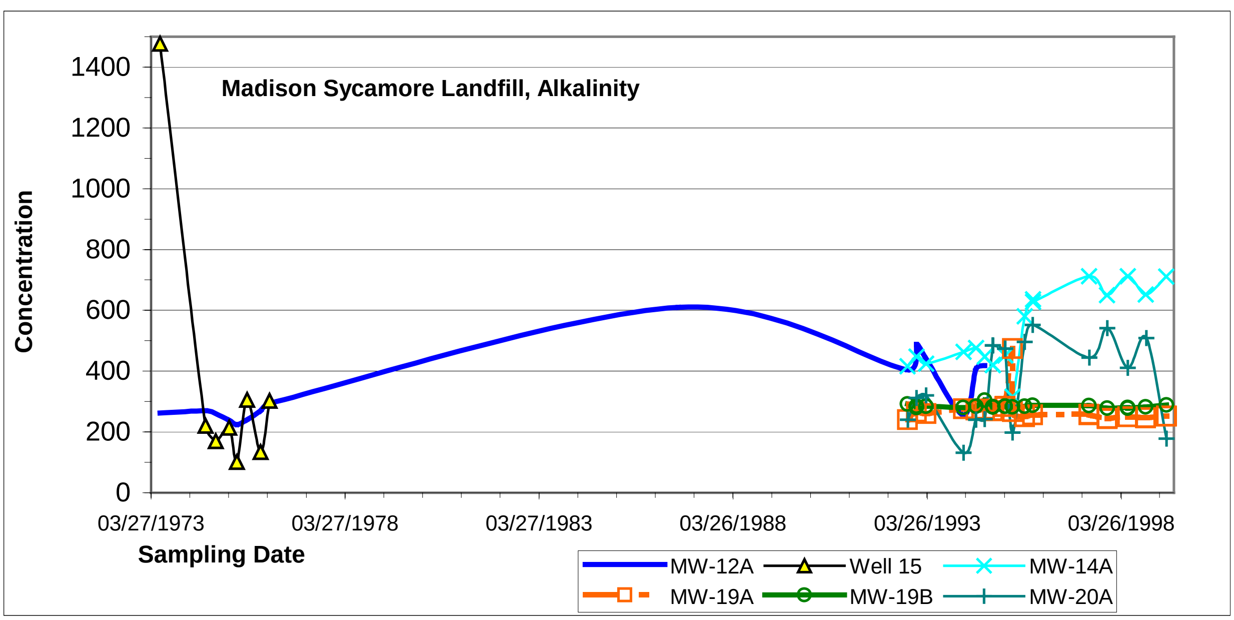


FIGURE 5B. CHLORIDE CONCENTRATIONS IN MADISON SYCAMORE LANDFILL MONITORING WELLS

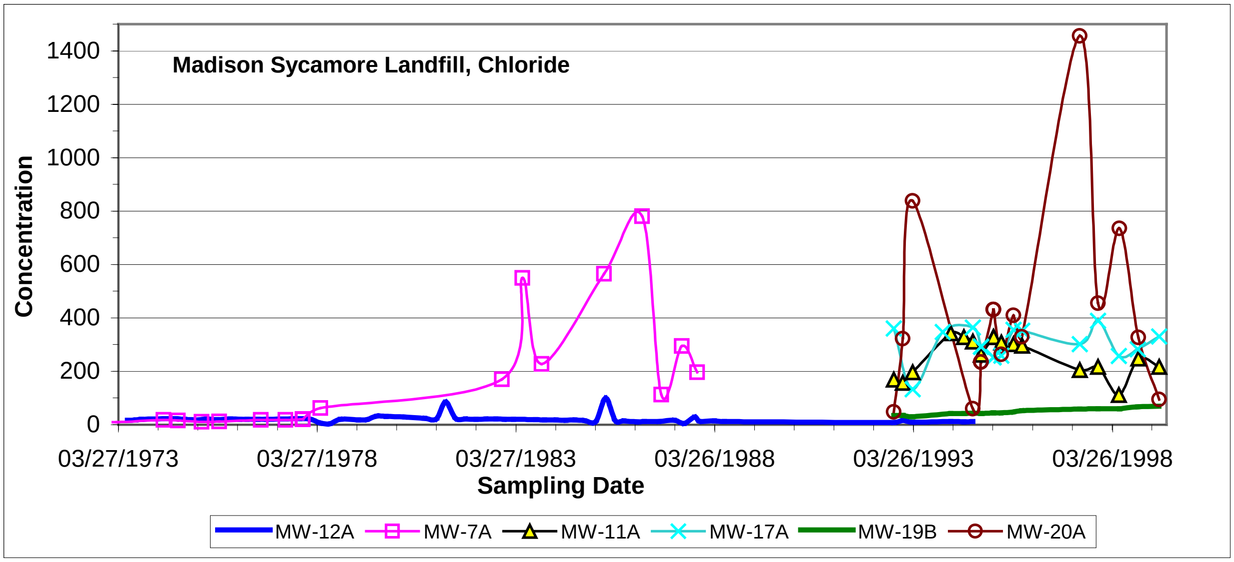



FIGURE 5C. COD CONCENTRATIONS IN MADISON SYCAMORE LANDFILL MONITORING WELLS

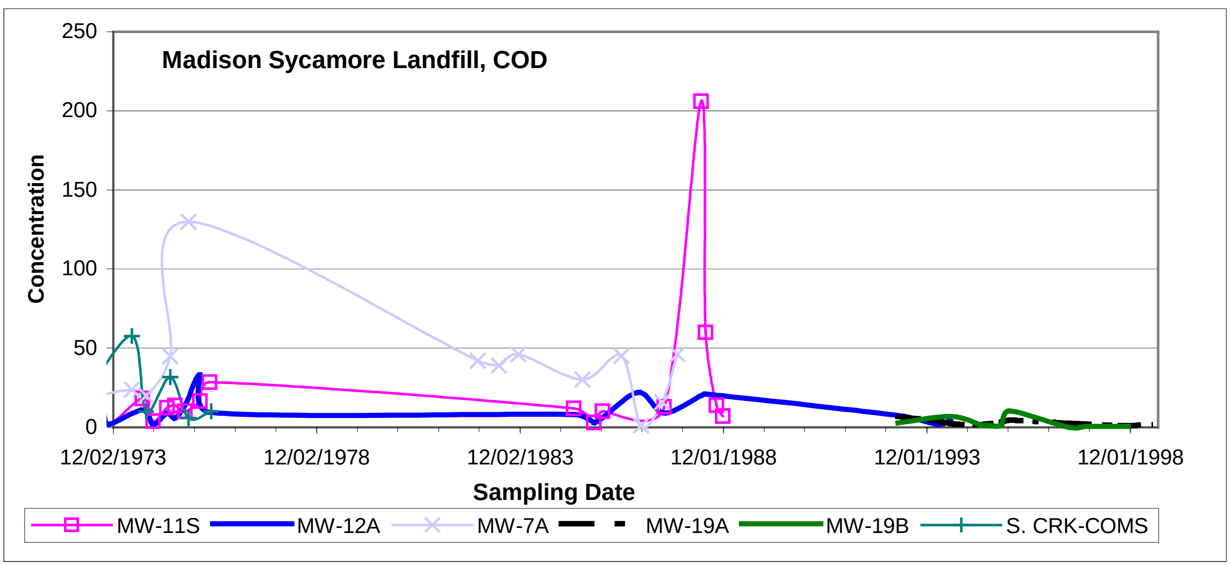


FIGURE 5D. CONDUCTIVITY IN MADISON SYCAMORE LANDFILL MONITORING WELLS

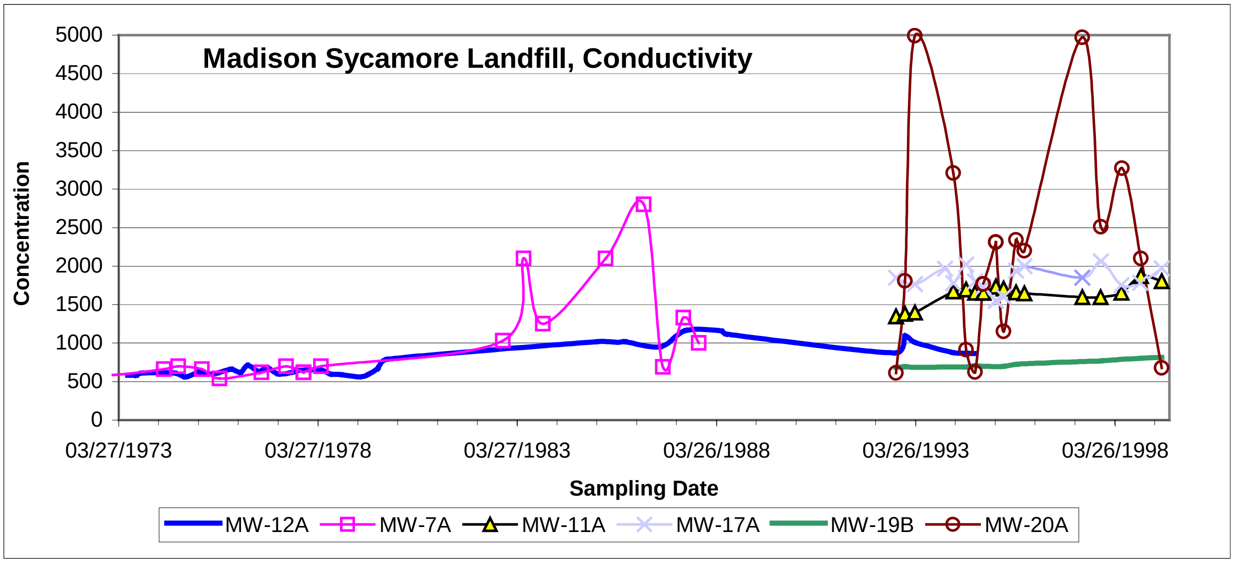
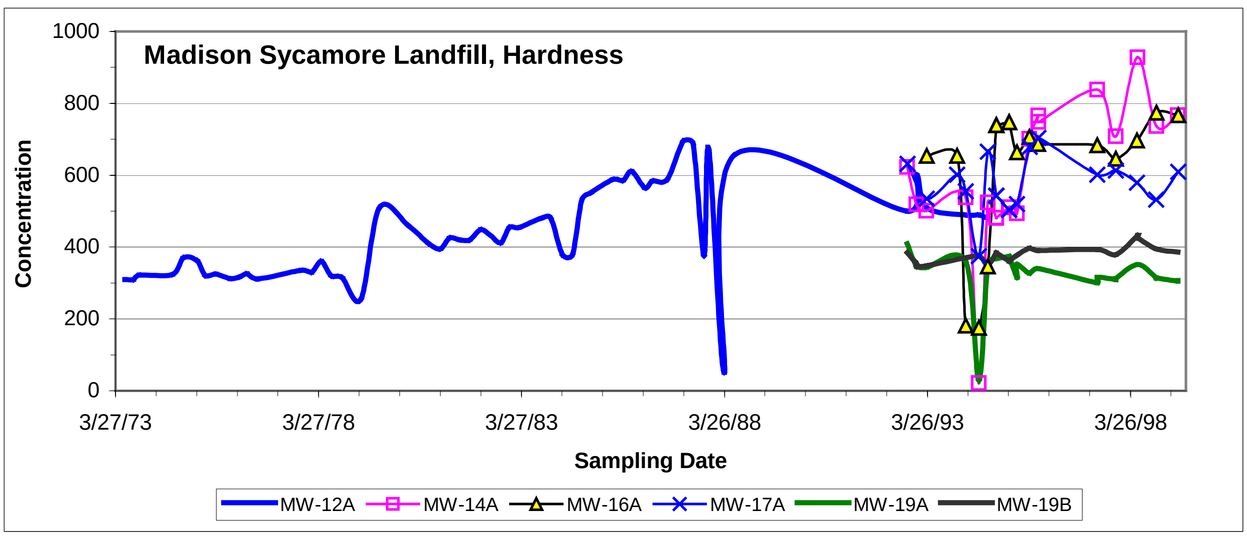



FIGURE 5E. HARDNESS CONCENTRATIONS IN MADISON SYCAMORE LANDFILL MONITORING WELLS




The box plots indicated an overall impact to groundwater; however, when investigators reviewed the time versus concentration graphs, the data were only somewhat useful. Even though an overall impact is seen for most of the parameters, the data is confusing because of frequent spikes and dips.

Figure 5A shows alkalinity data that was not very useful due to breaks in most of the data and no real significant impact between upgradient and downgradient wells. The data for chloride and conductivity show similar trends, with an increase in concentration around 1980, a drop around 1985, and high levels again starting around 1993, but no steady increase. Instead, the data jump around, making it difficult to draw any real conclusions about contamination at this site. COD data follows an almost opposite trend from chloride and conductivity. The data for COD is even more sporadic than the other data, but a few consistent data points around 1980-1985 and spikes above background make COD a somewhat useful parameter. Hardness data (Figure 5E) were not useful mainly because the upgradient wells show the same levels as the downgradient wells.

## COD Effectiveness by Landfill Type

Investigators categorized landfill assessments in the following waste types:

- Municipal Solid Waste (MSW),
- MSW Combustor Residue
- Paper Mill Sludge,
- Fly or Bottom Ash (from Utilities),
- Foundry Sand, and
- Demolition Waste.

Table 3 summarizes the assessments by landfill waste type. Investigators included VOCs in the overall effectiveness assessment because hydrogeologists in the Waste Management Program consider them as key parameters for identifying contamination, particularly when the patterns for the other indicators are confusing or do not clearly indicate that contamination is present. Twenty-eight (28) landfills tested groundwater samples for VOCs. Of those 28 sites, 24 had useful VOC data, one had data that was not useful, and three had insufficient data to drawn conclusions.

**Table 3. Summary totals for COD study criteria.**

| Type of Landfill | Total # Sites Evaluated | # Sites where COD useful / # Sites testing for COD | # Sites where Inorganic parameters useful / #Sites testing Inorganic parameters | # Sites where VOCs useful / # Sites testing for VOCs |
|---|---|---|---|---|
| MSW | **15** | 4 / 14 | 11 / 14* | 12 / 14 |
| Paper | **11** | 5 / 11 | 10 / 11 | 2 / 4 |
| Demolition | **5** | 1 / 5 | 5 / 5 | 4 / 4 |
| Foundry | **5** | 2 / 5 | 5 / 5 | 3 / 3 |
| Fly or Bottom Ash | **10** | 1 / 6 | 10 / 10 | 0 / 0 |
| MSW Combustor | **4** | 2 / 4 | 4 / 4 | 3 / 3 |
| **TOTALS:** | **50** | 15 / 45 | 45 / 49 | 24 / 28 |

* One MSW landfill was excluded from the data set.

### *Municipal Solid Waste (MSW) Landfills*

We examined groundwater data from fifteen municipal solid waste (MSW) landfills. In only 4 of the 15 MSW landfills, COD showed either an overall impact or a trend associated with the site's history. Inorganic indicator parameters were useful at detecting the contamination in 11 of the 15 sites. VOC data were even more helpful as the contamination was clearly shown in 12 of 14 landfills that tested for VOCs. At Refuse Hideaway, there was limited data available for the indicator parameters because once the contaminant plume was identified, remedial action focused on specific contaminants, not indicators. The data from this assessment was excluded from most further analyses.

**Table 4: Municipal Solid Waste Landfill Parameter Effectiveness Assessments**

| Landfill Name | Assessment |
|---|---|
| City of New Richmond | *COD Effective* / Inorganics Effective |
| Waste Control Inc. | *COD Effective* / Inorganics Effective |
| Juneau County | *COD Effective* / Inorganics Effective |
| Oconto Falls | *COD Effective* / Inorganics Ineffective |
| Village of Weston | *COD Somewhat / Inorganics Effective* |
| Sycamore | *COD Somewhat / Inorganics Somewhat* |
| City of Amery | COD Ineffective / *Inorganics Effective* |
| Metropolitan Refuse District Inc | COD Ineffective / *Inorganics Effective* |
| Town of Wheaton | COD Ineffective / *Inorganics Effective* |
| Town of Chase | COD Ineffective / *Inorganics Effective* |
| Town of Pound | COD Ineffective / *Inorganics Effective* |
| Marathon County | COD Ineffective / *Inorganics Effective* |
| Portage County | COD Ineffective / *Inorganics Effective* |
| Mineral Point (City of Madison) | COD Ineffective / *Inorganics Somewhat* |
| Refuse Hideaway | No COD Data / Inorganics Ineffective |

### *Paper Mill Sludge Landfills*

Of the eleven paper mill sludge landfills reviewed, COD was an effective parameter for almost half of the sites. Inorganic indicator parameters were effective for 10 of the 11 sites. At the remaining landfill, the inorganic parameters were *Somewhat Effective*. VOCs are not required monitoring at paper mill sludge landfills. At the two landfills that did monitor for VOCs, investigators noted PAL exceedances at both.

**Table 5: Paper Mill Sludge Landfill Parameter Effectiveness Assessments**

| Landfill Name | Assessment |
|---|---|
| Georgia Pacific Tomahawk Mill | *COD Effective / Inorganics Effective* |
| Consolidated Papers Inc. – Stevens Point | *COD Effective / Inorganics Effective* |
| Stora Enso North America – Water Quality Center | *COD Effective / Inorganics Effective* |
| Plainwell Tissue | *COD Effective / Inorganics Effective* |
| Flambeau Paper Corp | *COD Effective / Inorganics Effective* |
| Wausau Papers | *COD Somewhat / Inorganics Somewhat* |
| Appleton Papers | COD Ineffective / *Inorganics Effective* |
| H&R Paper & Refuse Service | COD Ineffective / *Inorganics Effective* |
| Badger Paper Mills | COD Ineffective / *Inorganics Effective* |
| Rhinelander Paper Pinelake | COD Ineffective / *Inorganics Effective* |
| Weyerhaeuser Co | COD Ineffective / *Inorganics Effective* |

### *Demolition Landfills*

Investigators reviewed data from five demolition landfills. COD was effective at only one site compared to inorganic parameters that were effective at all five sites. Monitoring for VOCs is required for demolition landfills; however, one landfill did not have VOC data in GEMS. At the four sites that monitored for VOCs, results indicated contamination.

**Table 6: Demolition Landfill Assessments**

| **Landfill Name** | **Assessment** |
|---|---|
| Oneida County | *COD Effective / Inorganics Effective* |
| Perrenoud | *COD Inffective / Inorganics Effective* |
| Madison Prairie | *COD Ineffective / Inorganics Effective* |
| Tri-County Disposal | *COD Ineffective / Inorganics Effective* |
| Portage County Demo | *COD Ineffective / Inorganics Effective* |

### *Foundry Landfills*

Five foundry landfills were reviewed and showed similar results to demolition landfills. COD was effective in 2 of the 5 sites, and other parameters were effective at all five sites.

**Table 7: Foundry Landfill Assessments**

| **Landfill Name** | **Assessment** |
|---|---|
| Kohler Company | *COD Effective / Inorganics Effective* |
| Badger Mining St. Marie | *COD Effective / Inorganics Effective* |
| Falk Corporation | *COD Ineffective / Inorganics Effective* |
| Waupaca Foundry | *COD Ineffective / Inorganics Effective* |
| Richland Center Foundry Company | *COD Somewhat / Inorganics Effective* |

### *Fly or Bottom Ash Landfills*

Ten fly or bottom ash landfills were reviewed for this study. Inorganic indicator parameters clearly detected the contamination in all 10 sites. Only one of the ten fly or bottom ash sites had effective COD data. Although four landfills did not monitor for COD, the data adds support to the conclusion that inorganic indicators are effective for this type of landfill.

**Table 8: Fly or Bottom Ash Landfill Assessments**

| Landfill Name | Assessment |
|---|---|
| WPSC Pullium | *COD Effective / Inorganics Effective* |
| WP&L Rock River | *COD Ineffective / Inorganics Effective* |
| WP&L Nelson Dewey | *COD Ineffective / Inorganics Effective* |
| WPSC Weston | *COD Ineffective / Inorganics Effective* |
| Dairyland Power Cooperative | COD Ineffective / *Inorganics Effective* |
| Consolidated Papers - Niagara | COD Ineffective / *Inorganics Effective* |
| WEPCO Cedar Sauk | No COD Data / *Inorganics Effective* |
| WP&L Columbia | No COD Data / *Inorganics Effective* |
| WP&L Edgewater 1-4 | No COD Data / *Inorganics Effective* |
| Dairyland Power Cooperative (?) | No COD Data / *Inorganics Effective* |

### *MSW Combustor Residue Landfills*

Four municipal solid waste combustor residue landfills were reviewed. However, none of these sites contain only MSW combustor residue. No landfills in Wisconsin accepted only MSW combustor residue. Therefore, the results of this study pertaining to MSW combustor residue may not be very accurate. COD was effective in two of the four sites, and other parameters were effective at all four sites. VOC data were generally helpful.

**Table 9: MSW Combustor Residue Landfill Assessments**

| Landfill Name | Assessment |
|---|---|
| BFI – Lake Area Disposal | *COD Effective / Inorganics Effective* |
| La Crosse County | *COD Effective / Inorganics Effective* |
| City of Sheboygan | *COD Ineffective / Inorganics Effective* |
| City of Wauwautosa | *COD Somewhat / Inorganics Effective* |

## Conclusions - Phases I and II

Based on the groundwater monitoring data reviewed for this study, the inorganic parameters alone or the inorganic parameters in combination with VOCs identify contamination from landfills more frequently than COD. This confirms staff reports that, in most instances, COD data is not used to detect contamination leaking from landfills. In only one case out of 50, the Oconto Falls landfill, was COD the primary indicator of contamination while most of the inorganic indicators were ineffective. At this site, groundwater monitoring began after WDNR observed an orange stream coming from the landfill into an adjacent cedar swamp.

VOCs were an important parameter for detecting contamination at many of the sites we studied. It is important to note that VOCs are required only at MSW landfills so, although we were able to evaluate VOC data for many of the sites in all but one category in this study, it may not be available generally. Although COD is an indicator of organic contaminants, the test is not designed to be a good indicator of VOC contamination. Samples for COD are not collected using the same precautions as VOCs (no sample agitation and placed in vials with zero headspace), samples may be held for up to 28 days prior to analysis, and detection limits are in the milligram per liter range compared to microgram per liter for VOCs. It is not surprising that COD results did not indicate organic contamination by VOCs. This was confirmed during our study. We saw landfills with PAL exceedances for VOCs for which the COD results were ineffective.

By necessity, this study design was biased. The investigators intentionally sought out landfills with known groundwater contamination problems. Under these circumstances, it is easier to discount the value of COD data. COD may be a more important parameter when the data for the inorganic parameters are less than clear, what we called *Somewhat Effective* or where VOC data are not available. At landfills with complex hydrogeology and confusing results, COD or an equivalent parameter may lend support to the decision that contamination is coming from the landfill. Based on our data set, contamination could have been missed at one out of 50 sites if COD data were eliminated.

The third phase of this study determined if other parameters such as dissolved organic carbon (DOC), manganese, and iron may be better tests for identifying both toxic and non-toxic organic material and the reducing conditions present at landfills. Recommendations for the study as a whole are provided after the Phase III Conclusions.

## Phase III

## Sample Selection

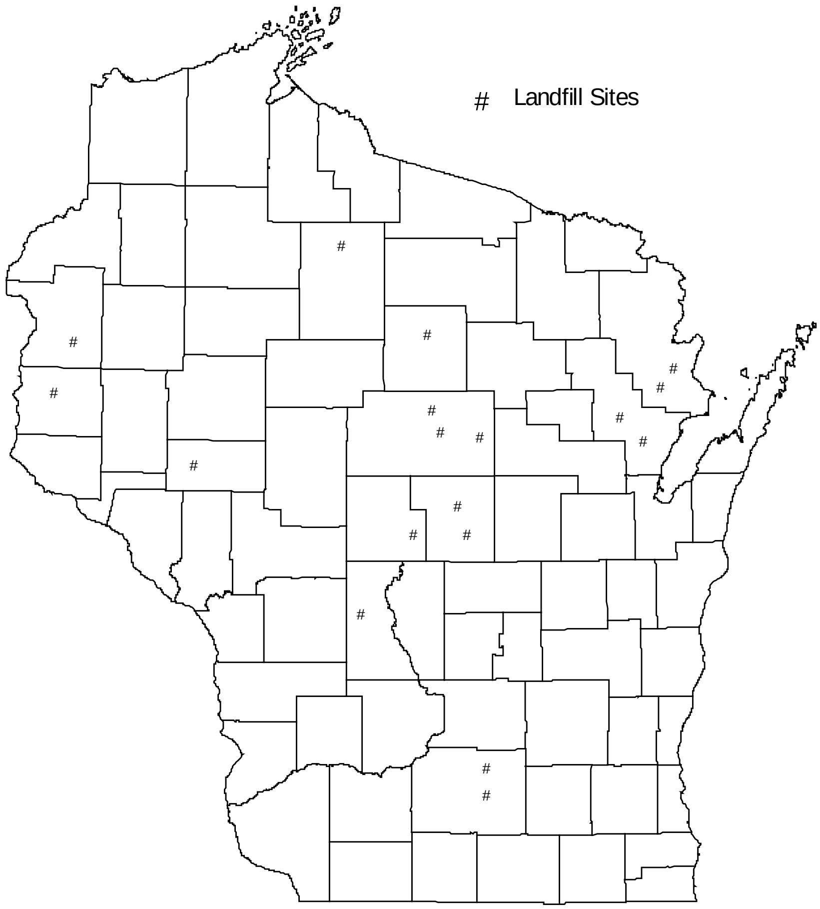
Twenty-four landfills were selected from the Phase II study as possible sites for groundwater sampling (Figure 6). These sites included (14) municipal solid waste, (6) paper mill, (1) demolition, (1) municipal solid waste combustor, (1) fly/bottom ash, and (1) foundry. Landfill types represented by only one site were deselected for statistical purposes, leaving municipal solid waste and paper mill landfills. Sampling arrangements were completed for eighteen of these remaining landfills including (12) municipal solid waste and (6) paper mill. Sample sites selected represent a wide range of construction techniques, soil types, drainage conditions, and degree of groundwater contamination. Table 10 lists the selected landfill names, type, upgradient and downgradient wells, and sample extraction technique. Sites have at least one upgradient and three downgradient wells. Downgradient well designations followed by a (L) indicate well locations that appear to be more lateral than downgradient of the landfill. These wells may still be good indicators of groundwater contamination due to mounding beneath landfills that often causes radial flow. Six sites use submersible or peristaltic pumps for sample extraction, the remaining twelve sites are bailed

**Table 10. Landfills selected for data analysis in Phase III. Table includes site and well names and sample extraction techniques.**

| Landfill Name | Landfill Type | Upgradient Wells | Downgradient/Lateral Wells | Sample Extraction Technique |
|---|---|---|---|---|
| City of Amery Landfill | MSW | MW1 | B2, G2, D2, B1, MW4R2(L) | submersible pumps |
| Tn. Chase | MSW | MW5A, MW5 | MW1(L), MW2, MW3 | bailers |
| Tn. Pound | MSW | UGW1 | SGW3(L), SGW6(L), DGW4, DGW5 | bailers |
| Village of Weston | MSW | MW14P | MW8P, MW8, MW7, MW9P | bailers |
| Sycamore Lf. (City Madison) | MSW | 23A | 14A, 14B, 18A, 18B | submersible pumps |
| Oconto Falls Landfill | MSW | B7, B4AR | B6, B6A, B7, B8, B8A, B12, B12A, B11 | bailers |
| Waste Control, Inc. | MSW | MW31 | MW1(L), MW2(L), MW6, MW7(L) | bailers |
| City of New Richmond | MSW | MW6 | MW1, MW3 | bailers |
| Juneau County Landfill (old) | MSW | DSMW3 | OW1, MW2(L), MW14A(L), MW14B(L) | bailers |
| Marathon County (closed) | MSW | R30 | R13, R37, R38A, R40 | bailers |
| Portage County MSW site | MSW | MW12 | 20P, 21, 23, 23P | submersible pumps |
| Mineral Pt. Lf (City Madison) | MSW | 11A | 5A, 5B, 10A, 10B | submersible pumps |
| Georgia Pacific Tomahawk Mill | Paper | 82WT | ST15, 44AR, 85WT, 85PS(L) | peristaltic pumps |
| CPI- Stevens Point | Paper | B1R, B26R | B21R, B27R, B30 | bailers |
| Cons Papers Water Quality Cntr (Ash, sludge) | Paper | MW31 | MW8R, MW9R, MW14, MW14A | bailers |
| Plainwell Tissue | Paper | MW18 | MW9, MW9A, MW17, MW17A | submersible pumps |
| Flambeau Paper Corp | Paper | FOW5 | MW7, B22, B22A, MW9DR | bailers |
| Wausau Papers | Paper | P17 | P8, P11, P23, P27 | bailers |

**(L) indicates monitoring wells that appear to be in more lateral or side-gradient than downgradient to flowpaths relative to landfill location.**

FIGURE 6 . MAP OF WISCONSIN SHOWING LOCATION OF LANDFILLS SAMPLED IN PHASE 3.




## Methods

### *Sampling Techniques*

Investigators made arrangements with landfill staff and consulting firms involved in routine groundwater monitoring to split samples during regularly scheduled spring and fall monitoring events. Wells were purged and sampled according to protocols established for each landfill. Sufficient sample was extracted for regular monitoring tests plus analyses involved in this study. Dissolved oxygen was measured down hole in each well following purging and sample extraction. Oxidation-reduction potential was measured immediately in extracted water at each well site. Samples were field-filtered in-line from the well or as soon as possible after removal utilizing positive or negative pressure filtering devices. Filtered samples were transferred immediately to properly preserved containers and placed on ice for transport to the laboratory. One duplicate sample and field blank were taken at each landfill.

### *Analytical Methods*

Analytical methods selected for this study along with method detection limits are listed in Table 11.

**Table 11. Methods, detection limits, and limits of quantitation used in the analysis of parameters.**

| ANALYSIS | METHOD | LIMIT OF DETECTION | LIMIT OF QUANTITATION |
|---|---|---|---|
| Eh | 2580 B (APHA 1995) | 1 mV | 1 mV |
| DO | 4500-O G (APHA 1995) | 0.1 mg/L | 0.1 mg/L |
| Fe | 3111 B (APHA 1995) | 0.02 mg/L | 0.07 mg/L |
| Mn | 3111 B (APHA 1995) | 0.005 mg/L | 0.017 mg/L |
| $NH_4$ | Lachate #10-107-06-2C equivalent to 4500-$NH_3$ G (APHA 1995) | 0.01 mg/L | 0.03 mg/L |
| COD | 5220 C (APHA 1995) | 3.0 mg/L | 10.0 mg/L |
| DOC | 5310 B (APHA 1995) | 0.3 mg/L | 1.1 mg/L |
| Mn III COD | HACH Mn III COD | 73 mg/L | 243 mg/L |

Oxidation-reduction potential (redox potential or Eh) was measured using a platinum indicator electrode coupled with a silver/silver chloride reference electrode. Electrodes were connected to a digital pH/millivolt meter capable of measuring a positive or negative response with a resolution of ± 1 millivolt. Prior to each day's use the meter was zeroed using a shorting lead and electrode response was checked against a standard Light's solution having a millivolt potential of + 475 @ 25° C. Electrode response was checked again at the end of each sampling day and recorded along with reference solution temperature. Deviation of more than 10 millivolts from the theoretical Eh standard value indicates electrode maintenance is required. Sample Eh potential was measured in a large mouth 250 ml plastic bottle fitted with a two-hole rubber stopper through which the electrodes were inserted. Measuring Eh in this completely filled and sealed container minimized air contact with the sample and helped reduce changes in the measured Eh value due to air oxidation. Monitoring well samples were placed immediately in the plastic bottle and allowed to come to equilibrium with gentle agitation. Eh values and temperature were recorded to the nearest millivolt and 0.1° C, respectively. A second sample aliquot was measured to ensure successive results were within ± 10 millivolts.

Investigators noted deterioration of Eh electrode response during the spring sampling event. Repeated attempts to clean the electrode surface failed to restore response and a new combination Eh electrode was ordered. The new electrode was not received until after the spring sampling period and consequently was first used during fall sampling. Data analysis took into account that different electrodes were used in the spring and fall events. Eh results from spring and fall sampling represent potentials of platinum electrode versus silver/silver chloride electrode and are not corrected to the potential of the standard hydrogen electrode.

Dissolved oxygen (DO) was measured with a membrane covered polarographic sensor with a built-in temperature correction. The digital meter was switched on and allowed to warm up for at least 15 minutes prior to probe air calibration in the field. Once calibrated, the meter was left on for the sampling day and checked periodically to verify calibration. Following well purge and sample extraction, the DO probe was carefully lowered into the well to avoid oxygen introduction and slowly moved up and down in the well screen. DO values were recorded after the meter stabilized. DO measurement accuracy is dependent on the amount of oxygen introduced during the bailing process and whether the electrode is poisoned by dissolved gasses such as hydrogen sulfide.

Iron (Fe), and to a lessor extent, manganese (Mn) oxidize rapidly to insoluble forms when subject to air contact, so in-line filtering from the well is the best way to prepare metal samples; however, this process was not available at most sites. In most situations samples were placed in a transfer bottle, capped with as little head- space as possible, and transported to filtration equipment. Fe and Mn samples were removed from monitoring wells, filtered through 0.45 μm pore size filter, acidified to a pH less than 2 with trace metal grade nitric acid as quickly as possible, and placed on ice in a cooler for transport. Laboratory analysis was accomplished using flame atomic absorption spectroscopy.

Ammonium nitrogen ($NH_4$) samples were filtered and preserved in a similar manner as metal samples except that the filtered sample was acidified to a pH of < 2 with ACS grade sulfuric acid. Preserved samples were stored at temperatures of 4° C or less and analyzed with a continuous flow auto-analyzer.

Chemical oxygen demand (COD) was analyzed from the same sulfuric acid preserved sample as ammonium. Two milliliters of sample or diluted sample were refluxed on a block digester in a closed vessel and titrated with standard ferrous ammonium sulfate. The COD method uses the chromate ion to oxidize organic compounds and reduced minerals. COD test results are, therefore, a measure of the combined oxygen consumption due to the oxidation of organic compounds plus reduced minerals and are given as mg/L of oxygen.

Dissolved organic carbon (DOC) samples, were field-filtered and placed in 60 ml glass vials with teflon lined caps. One filtered field balnk and duplicate sample was taken at each landfill using the contracting firm's filters, filtering apparatus, and de-ionized water. For the fall sampling, the EFT lab supplied ASTM type I water for rinsing filters and for blank water because the previous blanks were contaminated. In some cases, the contamination detected in the field blanks was much higher than up-gradient well results. Samples were placed in a cooler on ice and transported to the laboratory for analysis. Representative sample aliquots were transferred to clean auto-sampler vials, acidified to a pH < 2 with phosphoric acid, and purged prior to analysis. In this case, the analysis is more accurately called non-purgeable organic carbon (NPOC). The purging process also removes volatile organic matter from the sample. Purged samples were analyzed by the combustion-infrared method using an oxidative catalyst and high temperature. The resulting $CO_2$ is dried and measured by means of a nondispersive infrared detector. A dual range calibration curve was used, allowing a calibration range of 0 - 50 mg/L carbon.

The laboratory used filtered, sulfuric acid-preserved samples for the Hach Mn III COD method. Samples were filtered through a chloride removal cartridge prior to digestion to avoid potential chloride interferences. This non-mercury method uses the $Mn^{+3}$ ion to oxidize organic compounds and reduced minerals via a closed reflux digestion followed by colorimetric detection. The ETF lab was unable to obtain good sensitivity with this method and used it only on a few high COD samples to check method effectiveness in monitoring highly contaminated sites.

### *Statistics*

Investigators determined the relative strength of direct and inverse relationships by applying Pearson Correlation Coefficients to Hg COD and DOC results versus the various parameters. Results of paired data are included in tables, graphs, and texts. A few heavily contaminated sites that tend to skew correlations and mask potentially more important relationships in the lower concentration range dominate these data. The heavily contaminated sites have been eliminated from most correlations to reveal relationships at the break-through level. Data have been analyzed in a variety of subgroups including: spring up-gradient, spring down-gradient, fall up-gradient, fall down-gradient, paper mill, municipal solid waste, bailed wells, and pumped wells.

## Phase III Results

The primary objective of Phase III was to determine if an acceptable substitute analyte for Mercury COD was available for detecting early occurrence of leachate impacting groundwater.

We rejected the Hach chemical company Mn III COD early on in the project because of inadequate sensitivity for landfill monitoring. Hach states the method working range as 20 to 1000 mg/L, which indicates a much better detection limit than we were able to produce in the lab. ETF lab calculated its detection limit as 73 mg/L. The variability we observed was at least partially due to the chloride removal cartridge that caused erratic results most noticeable in the lower portion of the calibration curve. Samples selected for the Hg COD versus Mn III COD had Hg COD results of 100 mg/L or greater. Results correlated well to mercury-COD (Hg COD) at values over 100 mg/L. The Mn III COD method may have some use on heavily impacted groundwater but lacks the sensitivity to be a good indicator of initial breakthrough of leachate.

The chemical parameters used in this project included Hg COD, Dissolved organic carbon (DOC), Fe, Mn, Eh, NH4, Mn III COD, Conductivity, and Dissolved Oxygen. Hardness, alkalinity, and chloride analyses conducted by the consultants were not available for this data analysis. Each of these may be very useful in detecting leacheate reaching groundwater, as Phase II seemed to indicate.

Early results from this project indicated that the DOC analysis had the best probability of being a good substitute for Hg COD. Therefore, we highlighted it in this discussion and in the correlations of other parameters relative to that Hg-COD.

Correlation analyses between Hg COD and DOC and each of the other chemical parameters are presented in Table 13 for all data. In addition, data are separated by spring and fall sample periods, up- and down gradient wells and by Paper Mill and MSW sites. We evaluated the p values for each correlation coefficient to determine their significance at the .01 and .05 levels, and 99 and 95% confidence intervals, respectively. The numbers of samples used in each correlation analysis are included in Table 13. Tables 14 and 15 are the correlation matrix for the data sets presented in Table 13. Correlation coefficients for the relationship between each chemical analyzed and the associated p value can be found in these tables.

Data for sites with Hg COD values greater than 150 were excluded from this data analysis because they skewed the data and were not useful as early warning sites as they were already severely impacted. Figures 7 to 26 show relationships between Hg COD and DOC and the other chemical parameters graphically. Figures 7 to 13 present data for the 6 paper mill sites and 12 municipal sites. Figures 14 to 26 present data separated by both the spring and fall sampling periods and by up and downgradient wells. Each graph plots DOC or Hg COD against one of the other chemical parameters.

All raw data are presented in the Appendix as is a table of data from one ICP run on the data which presents metals data for a number of elements not originally part of the project. These are presented as they indicate some interesting values potentially useful in future discussions of landfill monitoring.

## Discussion

The data presented in Table 13 and in the following figures show many of the chemical parameters included as part of this project correlate well to both Hg COD and to DOC. The Pearson Correlation Coefficient is represented by an r-value ranging from 0.000 to $\pm$1.000. Correlations of r = 0.000 indicate a totally random distribution of points without any relationship between the dependent and independent variable. Positive r-values represent direct relationships and negative r-values indicate inverse relationships. Generally, correlations of $\pm$0.400 can indicate a strong relationship for environmental prameters; however, for reguatory purposes, a correlation of 0.600 or better may be in order. In addition to r-values, distribution of data, presence of outliers, and number of samples must be considered when evaluating relationships that are due to landfill impacts. Graphs for each parameter and for the up-gradient and down-gradient wells reveal considerable variability between sites and between seasons as represented by the two data sets.

### *Mercury Chemical Oxygen Demand vs Dissolved Organic Carbon*

The correlation's between Hg COD and DOC were the best found for this project and are shown in Table 13 and Figures 7 and 14. The greater sensitivity of the DOC method and its lack of any toxic waste should make it a very good substitute for the COD method. DOC values while more sensitive are often two to three times lower than COD due to the lack of inclusion of reduced metals in the DOC test. The figures and correlation coefficients indicate a slightly better relationship for paper mill sites than for municipal sites. The reason for the better correlation for the fall set of samples is unknown. There were several sites with high concentrations of both DOC and Hg COD in upgradient wells, which indicates some local impacts to groundwater other than the landfill. This makes the use of these and several other parameters related to oxygen and redox conditions more difficult for evaluating landfill impacts and reinforces the need for using multiple parameters and comparing changes over time to clearly identify landfill impacts.

It should be noted that spring field blanks were high, in some cases considerably higher than upgradient wells. Spring field blanks were prepared by running rinse water supplied by the contractors or landfill personnel through the same filtering and preservation process as samples. In the case of DOC field blanks, filtered rinse water was placed in 60 ml screw cap vials with teflon liners. Fall sampling was modified to include ASTM type I water supplied in a glass bottle with teflon lined screw cap for DOC field blanks. This water was used at most fall sampling sites. Table 12 compares statistics of spring and fall field blanks. Discarding the field blanks from the two fall sites using contractor's rinse water would lower the fall blank mean to near detection limits. This would indicate that the rinse water and not the filters or filtering devices were responsible for field blank contamination.

**Table 12. Mean, maximum, minimum, and standard deviation of DOC field blanks.**

| | DOC Field Blank Statistics mg/L | | | |
|---|---|---|---|---|
| | Mean | Std. Dev. | Min. | Max |
| Spring | 4.57 | 4.91 | 0.15 | 15.4 |
| Fall | 0.96 | 1.55 | 0.15 | 5.8 |

Poor quality rinse water had a significant effect on field blanks but may not have affected monitoring well water to the same extent if filters were well rinsed with sample prior to filling DOC vial. Fresh high quality de-ionized water in clean containers will be required for sample preparation if DOC becomes a required test parameter.

***Iron***

Correlations between Iron and DOC and Hg COD are presented in Table 13 and Figures 8, 15 and 21. Correlation coefficients between iron and other chemical parameters can be found in Tables 14 and 15. Iron (Fe) is second only to DOC with respect to Hg COD correlations. The effects of reducing conditions and the conversion of insoluble ferric hydroxides ($Fe+3$) to soluble ferrous iron ($Fe+2$) is well documented. This process makes Fe analysis a good consideration for landfill indicator status. Fe analysis by ICP-OES or AA is quick, sensitive, and relatively inexpensive. Due to the relatively rapid oxidation of ferrous iron it is important that monitoring wells be bailed with as little introduction of oxygen as possible and water samples be filtered and acidified immediately upon collection. Additional limitations of this method may include the presence of a strongly reduced substrate under the landfill having most of the iron previously removed from the mineralogy or natural reducing conditions resulting in high dissolved iron concentrations that would mask early leachate break through

There is considerable scatter shown on Figures 15 and 21, indicating a wide range of iron occurrence in both upgradient and downgradient wells. The occurrence of high concentrations of iron in some upgradient wells indicates reducing conditions in some sites where there was also higher than normal COD and DOC. Correlations between iron and DOC are much weaker than for Hg COD, which should be expected, as the Hg COD test would include iron while DOC does not. There is still a fairly good relationship at many sites as high DOC results in low oxygen and soluble iron.

### *Manganese*

Manganese (Mn) like iron becomes increasingly soluble as reducing conditions increase. Manganese may show up sooner at some sites than iron as it is converted from MnIV to the soluble MnII oxidation state at higher redox potential than is the conversion of FeIII to FeII. Correlation coefficients between Hg COD and Manganese were not as high as for iron but still significant at the .01 level except for fall upgradient wells significant at the .05 level. The correlation to MSW sites was not significant. Manganese correlations to DOC were all significant at the .01 or .05 level except for spring upgradient wells and the MSW sites.

As with iron, there were a number of sites where there was very little manganese found even though high concentrations of Hg COD or DOC were present. These sites may have very little iron or manganese in the local mineralogy or it is possible that these metals have been leached out if anoxic conditions have existed for many years. It appears that neither of these metals is a good substitute for Hg COD or DOC at all sites and alone would not be good early indicators of groundwater contamination.

### *Dissolved Oxygen and Eh*

Data showing relationships between DOC and Hg COD and the DO and Eh values are found in Tables 13 through 15 and in Figures 10, 11, 17, 18, 23, and 24. Correlations between DO and Eh and the other chemical parameters are found in Tables 14 and 15.

There should be a good relationship between oxygen and Eh for monitoring wells as the Eh is highly dependent on oxygen. This relationship was found to be generally very good, however the DO data often showed more oxygen to be present than was possible with the high dissolved metals and low Eh reading. This indicates some oxygen was contaminating samples as part of the sampling procedure, most likely during well development. If oxygen is contaminating the well the Eh measurements will also be affected, as will the iron data. This is further discussed in the methods section. In spite of these apparent measurement problems there were some good correlation's between Eh and the NH4, iron, and manganese data as well as for the DOC and Hg COD measurements. The apparent errors are relatively small and do not affect the trends of the data as much as the actual concentrations.

Both DO and Eh correlated well to both Hg COD and DOC making them useful for landfill monitoring. They are however both sensitive to sampling errors and need accurate field calibration to make them most useful.

### *Conductivity*

Conductivity is a simple, inexpensive field test that is most effective as an early indicator of contaminant impact, provided it is compared to prior data to detect trends. Conductivity is a measure of a liquid's ability to conduct an electric current and gives an indication of the total dissolved ions. It does not help determine specific contaminants and would not be a good indicator of trace organic compounds. Conductivity data is presented in Tables 13 through 15 and in Figures 12, 19, and 25. The graphs show a high amount of scatter with resulting correlation coefficients being insignificant for several of the correlations to Hg COD and DOC. All correlations were positive showing a general increase in conductivity with increases in Hg COD and DOC. The best correlations were for paper mill sites, which tended to have greater impacts on conductivity.

Correlation coefficients between conductivity and pH, Eh, and ammonium ($NH_4$) were good. The pH correlation is related to the trend for more mineralized water to have higher pH due to higher alkalinity values. Good correlations to Eh and ammonium indicate a relationship between contaminated wells and higher conductivity. The wide range of natural conductivity at different sites results in the wide range of scatter and emphasizes the need to use conductivity data on a site specific basis and along with others parameters to detect if change is occurring over time.

### *Ammonium*

Ammonium is correlated strongly to Hg COD and slightly less strongly to DOC especially at the MSW sites. These data are presented in Tables 13 through 15 and Figures 13, 20, and 26. Only one upgradient well had any significant NH4 which is not unusual, as ammonium is not often found in naturally occurring groundwater. This fact helps make NH4 a good indicator parameter. Ammonium also correlates well to Eh, Fe, Mn, and conductivity, showing it to relate well at sites where oxygen is depleted. It did not show up at all sites and we cannot tell from the data how soon it shows up in a contaminated well. It made a good indicator, but as with many other parameters, cannot be used alone as an indicator of contamination at all sites.

### *ICP Analysis for Other Chemicals*

The fall 2000 set of samples, run using an ICP analysis, shows some interesting results. No elevated concentrations were found for lead or copper and only slightly elevated concentrations of zinc were found. Several sites did, however, have elevated concentrations of sodium, potassium and total sulfur. These elements could be correlated to the other site information to see if they may make useful indicators. Sulfur numbers of several hundred were found at some sites.

### *Differences Between MSW and Paper Mill Sites*

Correlations between parameters are separated by paper mill sites and MSW sites on Tables 14 and 15 and in Figures 8 through 13. Most of the correlations between chemicals were similar for both data sets. There was somewhat less scatter in the paper mill data in a number of the figures indicating potentially more uniformity in the type of groundwater contamination under these sites compared to municipal sites.

**Table 13. Pearson correlation coefficients for test parameters by various sub-groups.**

**Mercury COD vs Test Parameters**

| Analyte or Parameter | All Sites | Spring Up | Spring Down | Fall Up | Fall Down | Paper Mill | MSW |
|---|---|---|---|---|---|---|---|
| **DOC** | 0.810 | 0.550 | 0.760 | 0.834 | 0.953 | 0.895 | 0.681 |
| **Fe** | 0.600 | 0.745 | 0.684 | 0.365 | 0.559 | 0.519 | 0.698 |
| **Mn** | 0.387 | 0.575 | 0.442 | 0.553 | 0.383 | 0.494 | 0.134 |
| **Eh** | -0.433 | -0.246 | -0.339 | -0.492 | -0.522 | -0.532 | -0.364 |
| **$NH_4$** | 0.485 | 0.744 | 0.542 | 0.732 | 0.436 | 0.562 | 0.229 |
| **Mn III COD** | -0.326 | | -0.331 | | | 0.825 | |
| **Cond.** | 0.354 | 0.084 | 0.451 | 0.347 | 0.250 | 0.663 | 0.279 |
| **DO** | -0.328 | -0.397 | -0.272 | -0.402 | -0.295 | -0.356 | -0.311 |
| **Number of Samples** | 144 - 158 | 16 - 18 | 41 - 48 | 14 - 17 | 53 - 57 | 47 - 51 | 94 - 106 |

**DOC vs Test Parameters**

| Analyte or Parameter | All Sites | Spring Up | Spring Down | Fall Up | Fall Down | Paper Mill | MSW |
|---|---|---|---|---|---|---|---|
| **Fe** | 0.307 | 0.343 | 0.318 | 0.476 | 0.341 | 0.275 | 0.364 |
| **Mn** | 0.280 | 0.296 | 0.302 | 0.483 | 0.272 | 0.456 | 0.147 |
| **Eh** | -0.333 | -0.151 | -0.286 | -0.480 | -0.404 | -0.393 | -0.295 |
| **NH4** | 0.316 | 0.362 | 0.433 | 0.510 | 0.294 | 0.611 | 0.074 |
| **Mn III COD** | -0.313 | | -0.760 | | | -0.840 | -0.794 |
| **Cond** | 0.256 | 0.201 | 0.461 | 0.353 | 0.109 | 0.739 | 0.070 |
| **DO** | -0.285 | -0.091 | -0.215 | -0.626 | -0.241 | -0.328 | -0.249 |
| **Number of Samples** | 134 -147 | 14 - 16 | 39 - 42 | 13 - 16 | 51 - 55 | 44 - 47 | 88 – 99 |

## Conclusions – Phase III

1. The Dissolved Organic Carbon method appears to be an excellent replacement method for Hg COD. It has greater sensitivity and correlates well to most other pollution indicators used in this study.
2. The Hach Mn III method is only useful for high COD samples exceeding 75 mg/l and would not be appropriate as an early contaminant plume detection method.
3. Both iron and manganese correlated well to Hg COD and fairly well to DOC. DOC does not include reduced metals as does the Hg COD test, resulting in lower numerical values for DOC. There is insufficient data from this study to evaluate how soon these reduced metals show up as a contaminant plume develops. They are good indicators of reducing conditions but elevated concentrations were not always found in downgradient wells. Differences in mineralogy and history of reducing conditions at a site can cause wide variability in the occurrence of these metals.
4. Dissolved oxygen and Eh (Redox potential) were both highly correlated to DOC and Hg COD even though there were some problems with oxygen contamination of wells during bailing. These field methods are useful in detecting reducing conditions that are often the result of contamination.
5. Several sites used in this study had anoxic water in upgradient wells with elevated concentrations of DOC, iron, and manganese apparently due to natural conditions. These parameters alone do not indicate a contaminant plume emphasizing the need for background data before the site is developed.
6. The case studies from Phase I of this project suggest that alkalinity changes over time may be an excellent early indicator of leachate reaching groundwater.
7. The ICP data run on one batch of samples would suggest that sodium, potassium and sulfate may be useful indicators at a number of sites.

## Recommendations – Based on Information from Phases I, II and III

## Implementation

1. WDNR should modify its rules so that COD is no longer required as part of routine detection groundwater monitoring for municipal solid waste landfills where VOC data is part of the routine detection monitoring program for groundwater.

2. WDNR should modify its rules so that COD is no longer required as part of routine detection groundwater monitoring for fly ash or bottom ash landfills because inorganic parameters are effective for detecting contamination.

3. For paper mill, foundry, and demolition landfills, WDNR should modify its rules for detection monitoring. At a minimum, the requirements should be adjusted to replace COD with Dissolved Organic Carbon (DOC). WDNR may need to consider phasing in the replacement to minimize the loss of historical monitoring data.

4. Prior to the rules being changed, WDNR should allow landfills to modify their sampling plans to substitute DOC for COD in routine groundwater sampling.

## Further Study

5. WDNR should evaluate whether similar comparisons can be made between results for COD and DOC or TOC in leachate. If comparisons are favorable, then the substitution should be made.

6. WDNR should consider a follow-up study to evaluate whether to add VOCs to monitoring requirements for demolition, foundry and paper mill sludge landfills.

7. The chloride, hardness, and alkalinity data collected by consultants at the studied landfills could be correlated to the data set developed for this project to determine how well these parameters correlate to those used in this project.

FIGURE 7. CORRELATION OF COD VERSUS DOC FOR ALL SAMPLED LANDFILLS, MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.

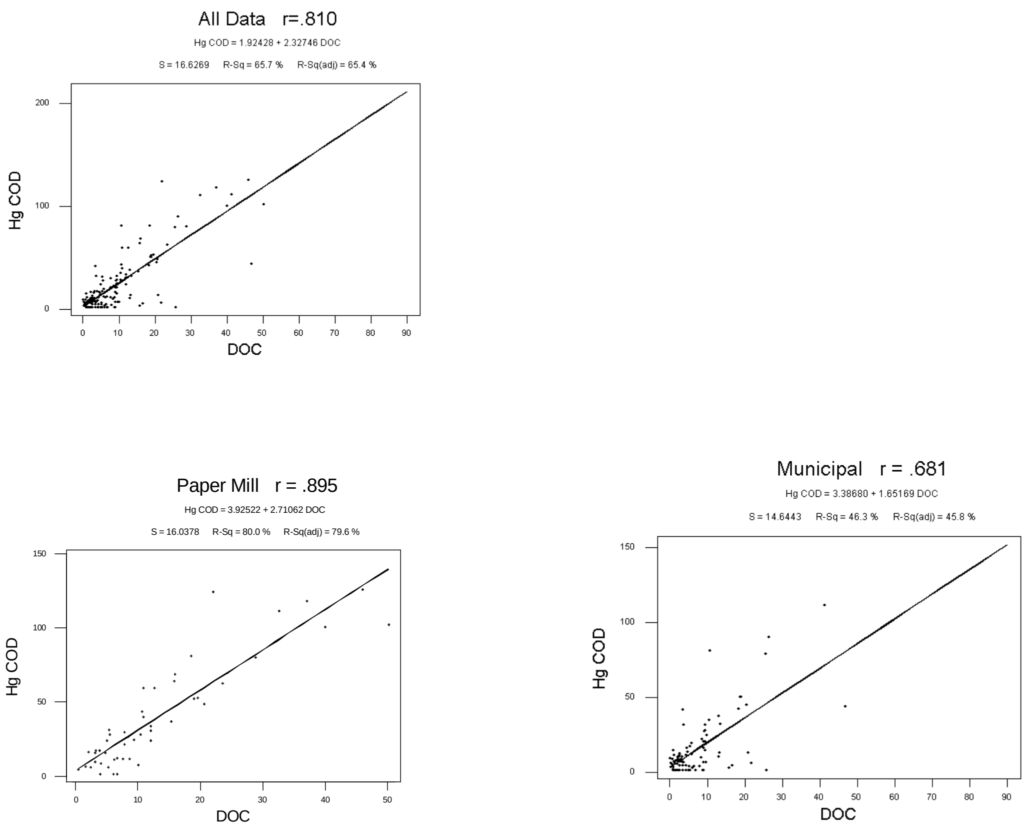


FIGURE 8. CORRELATION OF COD VERSUS MANGANESE AND DOC VERSUS MANGANESE FOR ALL SAMPLE LANDFILLS , MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.

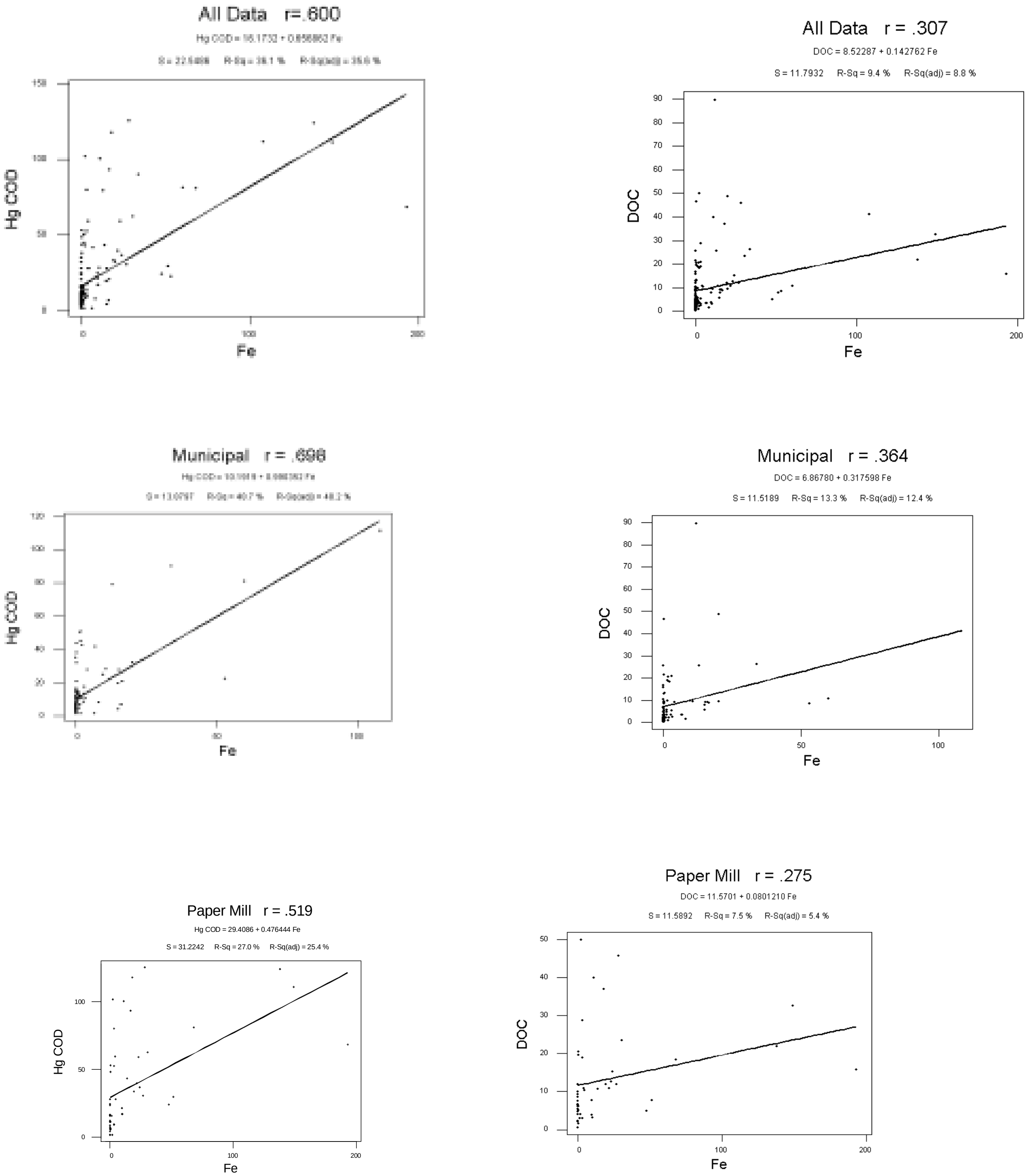


FIGURE 9. CORRELATION OF COD VERSUS MANGANESE AND DOC VERSUS MANGANESE FOR ALL SAMPLE LANDFILLS , MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.

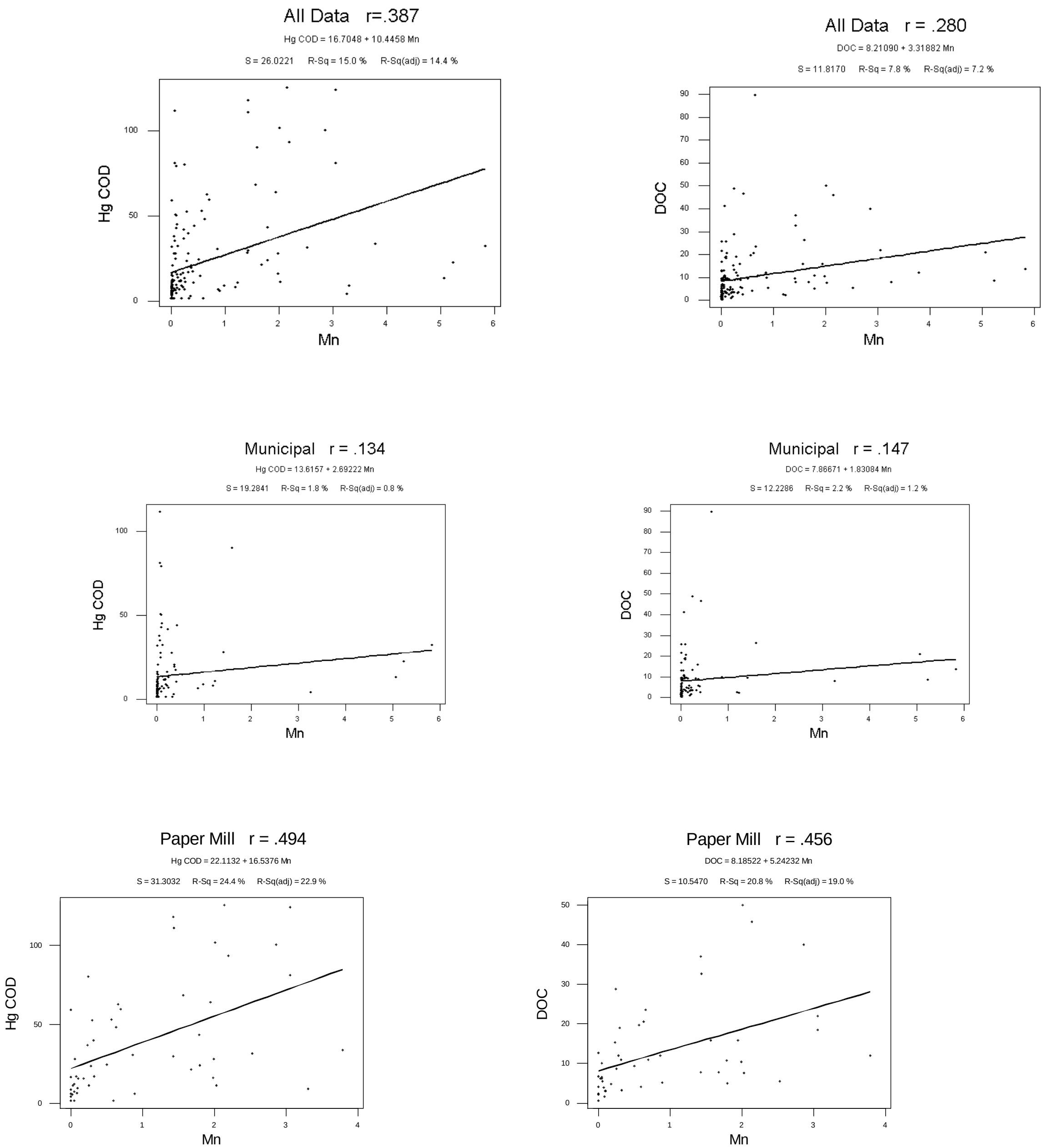
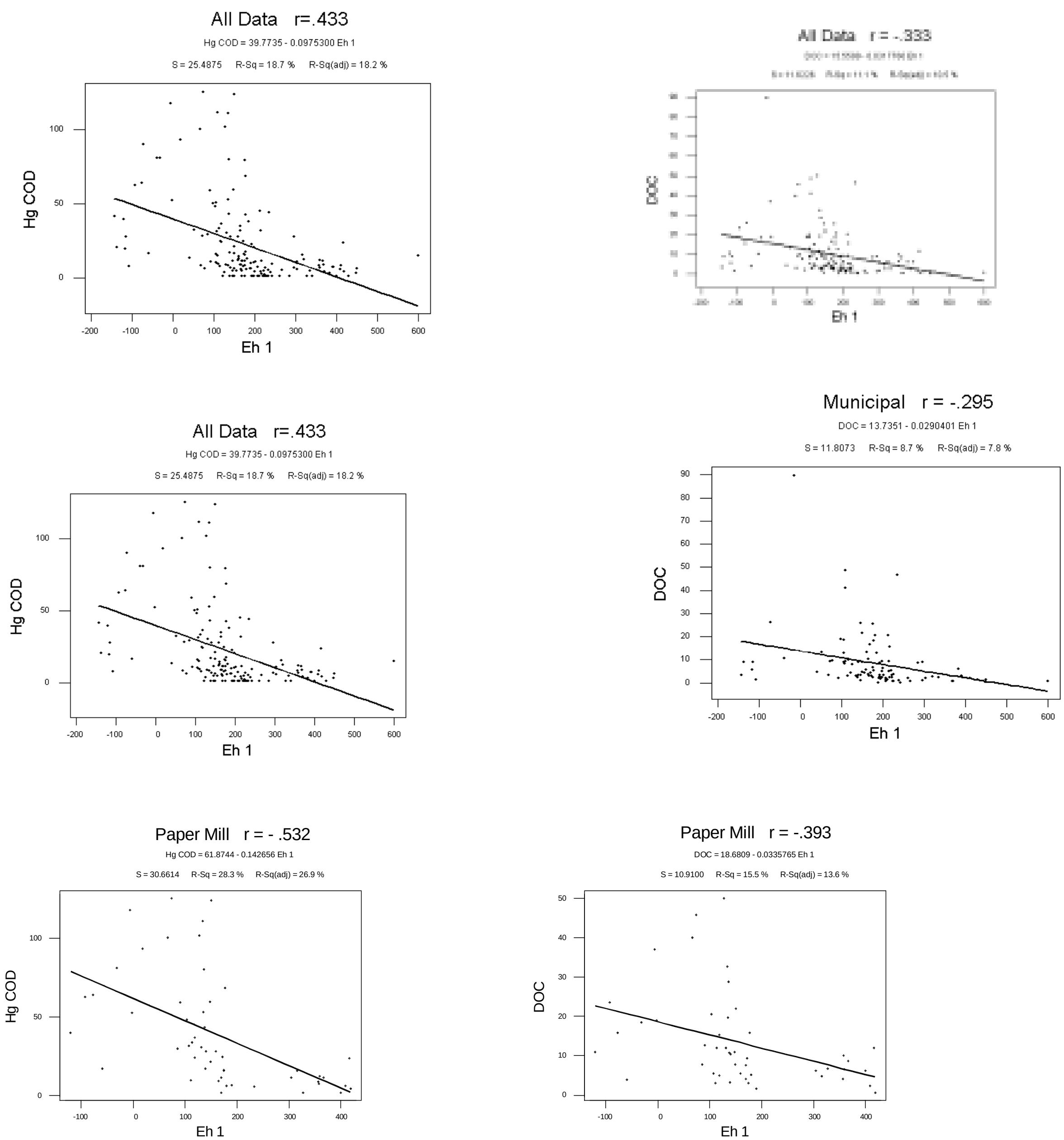
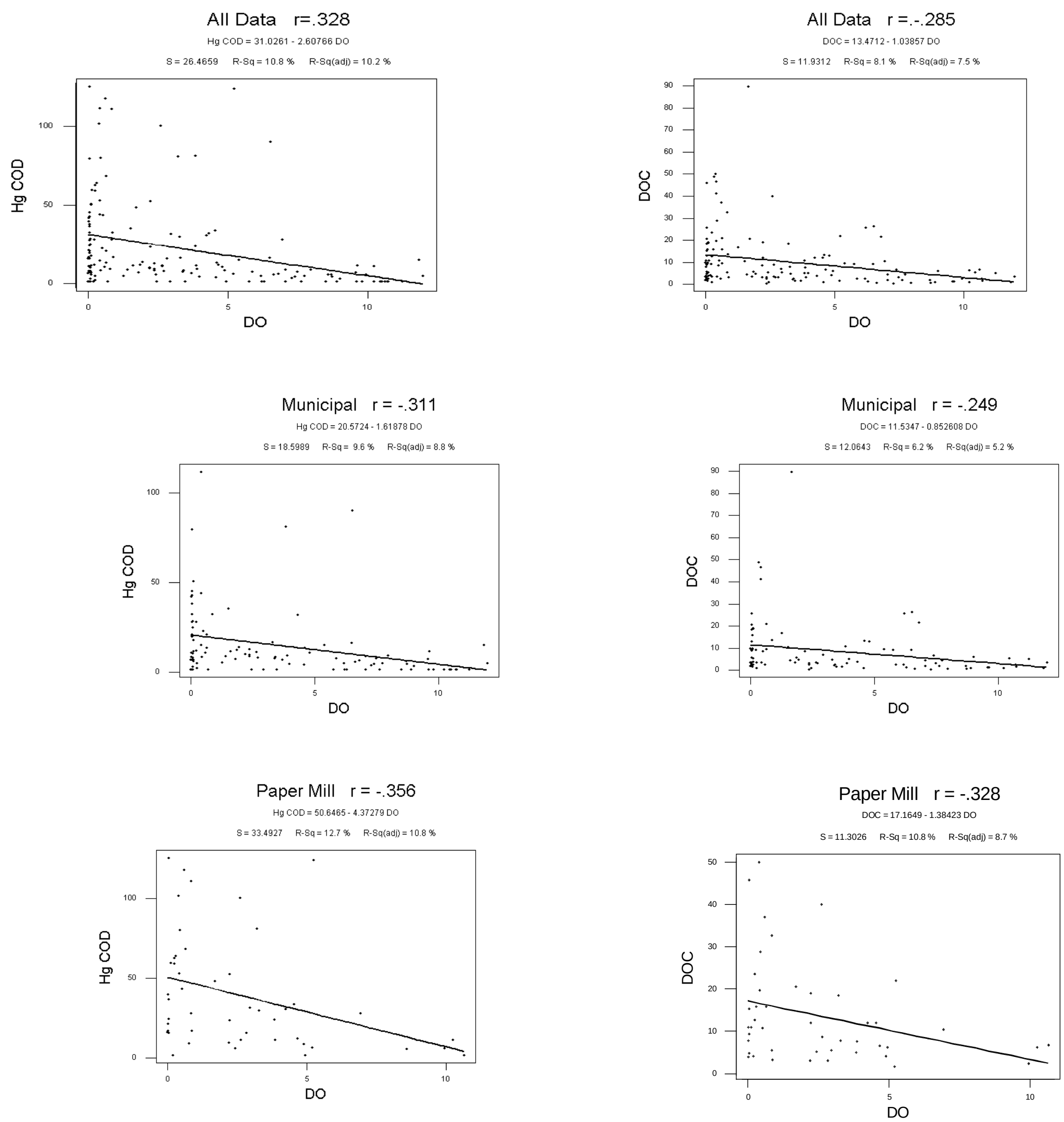


FIGURE 10. CORRELATION OF COD VERSUS EH AND DOC VERSUS EH FOR ALL SAMPLE LANDFILLS, MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.




Note: All correlation coefficients or "r" values should be negative.

FIGURE 11. CORRELATION OF COD VERSUS DO AND DOC VERSUS DO FOR ALL SAMPLE LANDFILLS, MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.




Note: All correlation coefficients or "r" values should be negative.

FIGURE 12. CORRELATION OF COD VERSUS CONDUCTIVITY AND DOC VERSUS CONDUCTIVITY FOR ALL SAMPLE LANDFILLS , MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.

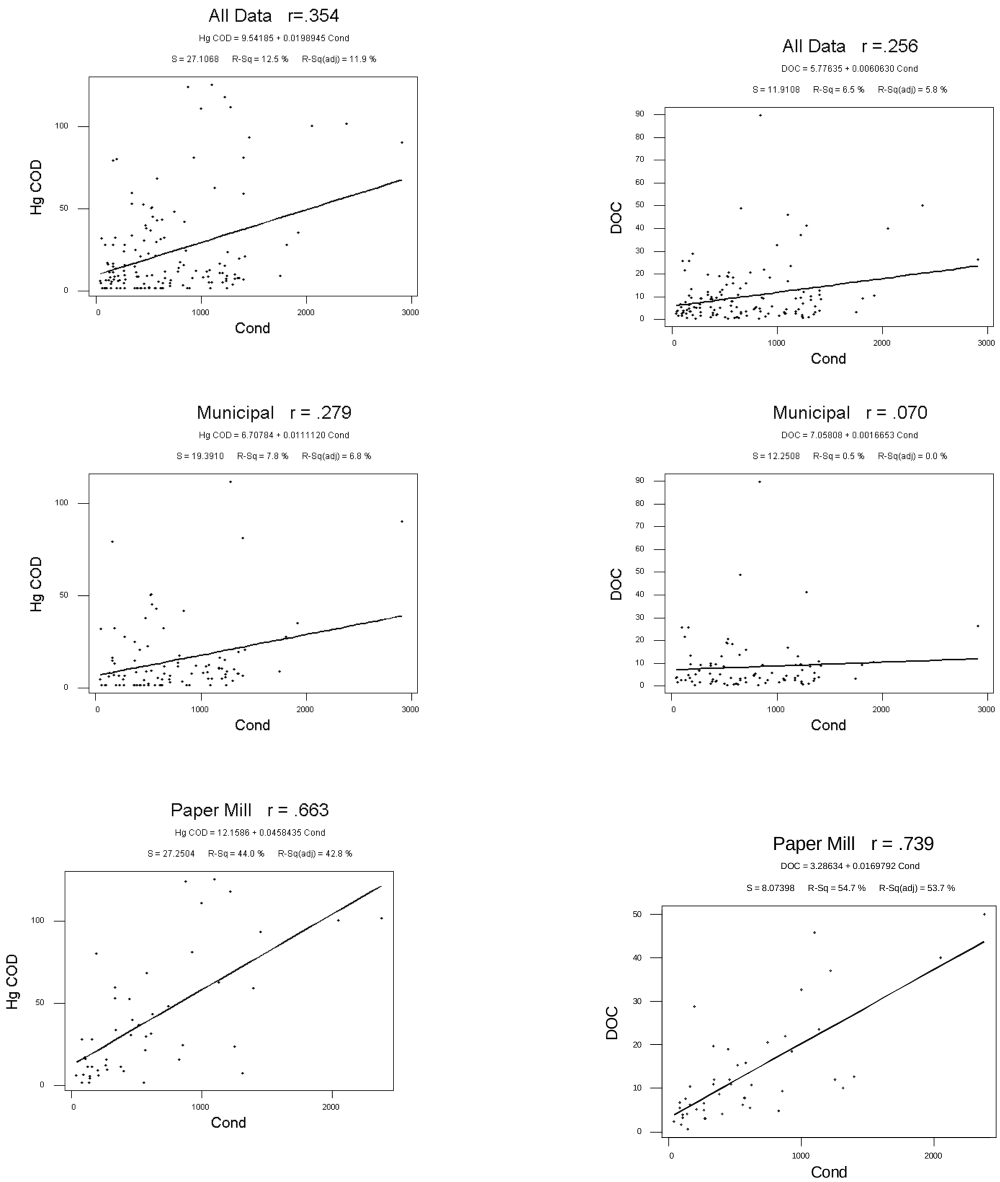


FIGURE 13. CORRELATION OF COD VERSUS AMMONIUM AND DOC VERSUS AMMONIUM FOR ALL SAMPLE LANDFILLS , MUNICIPAL LANDFILLS, AND PAPER MILL LANDFILLS.

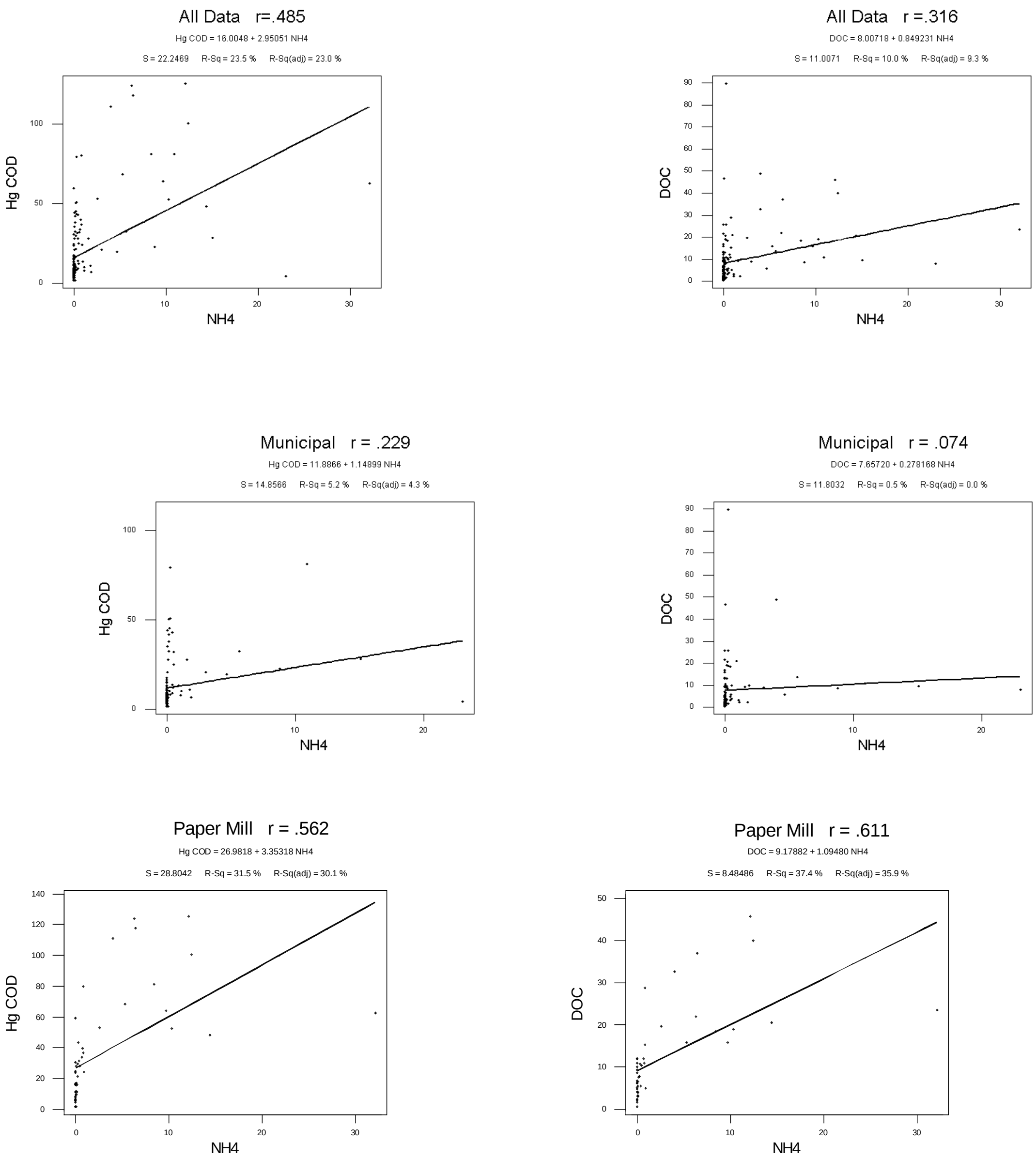


FIGURE 14. CORRELATION OF COD VERSUS DOC FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES

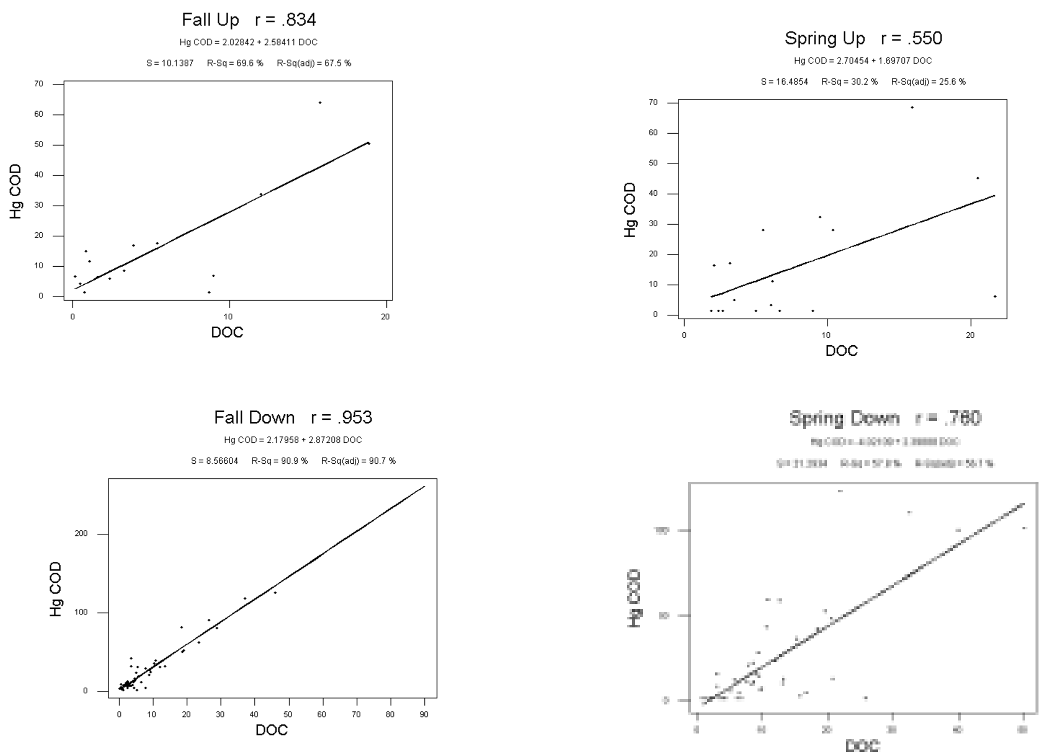



FIGURE 15. CORRELATION OF COD VERSUS IRON FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES

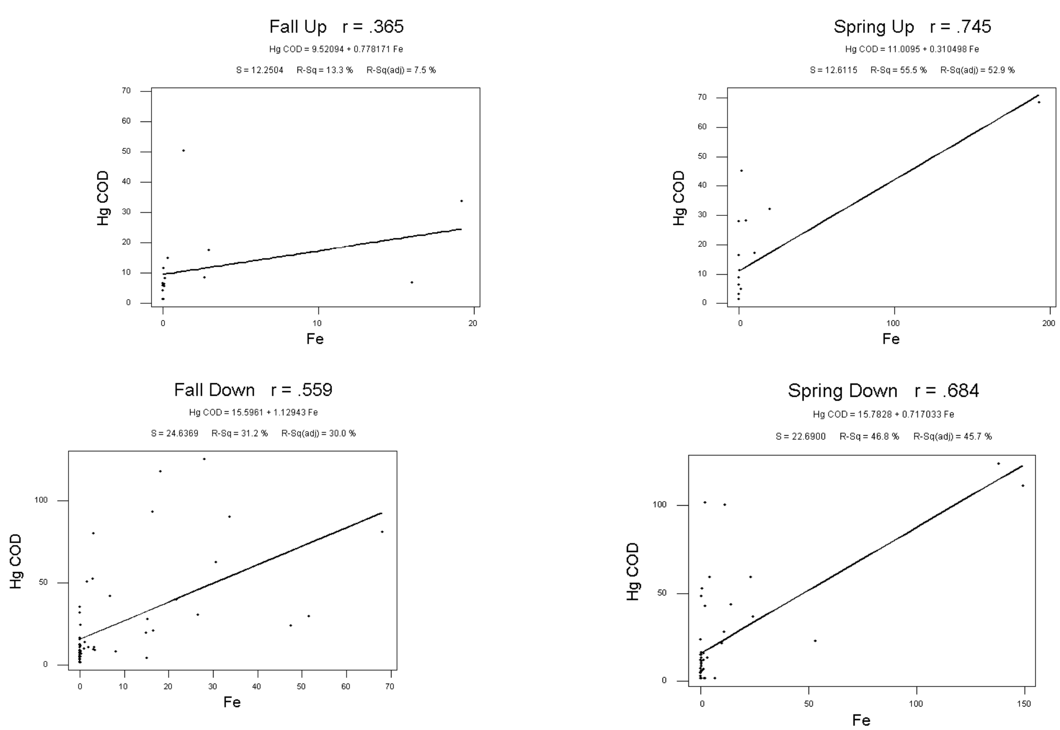


FIGURE 16. CORRELATION OF COD VERSUS MANGANESE FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

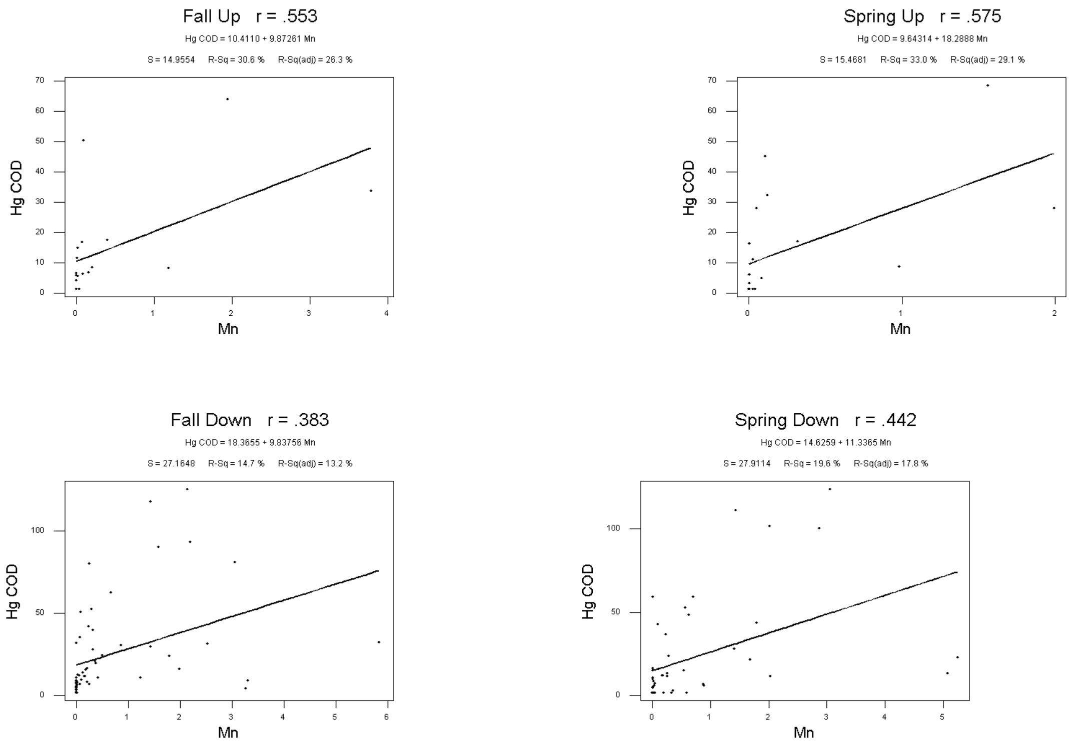



FIGURE 17. CORRELATION OF COD VERSUS EH FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

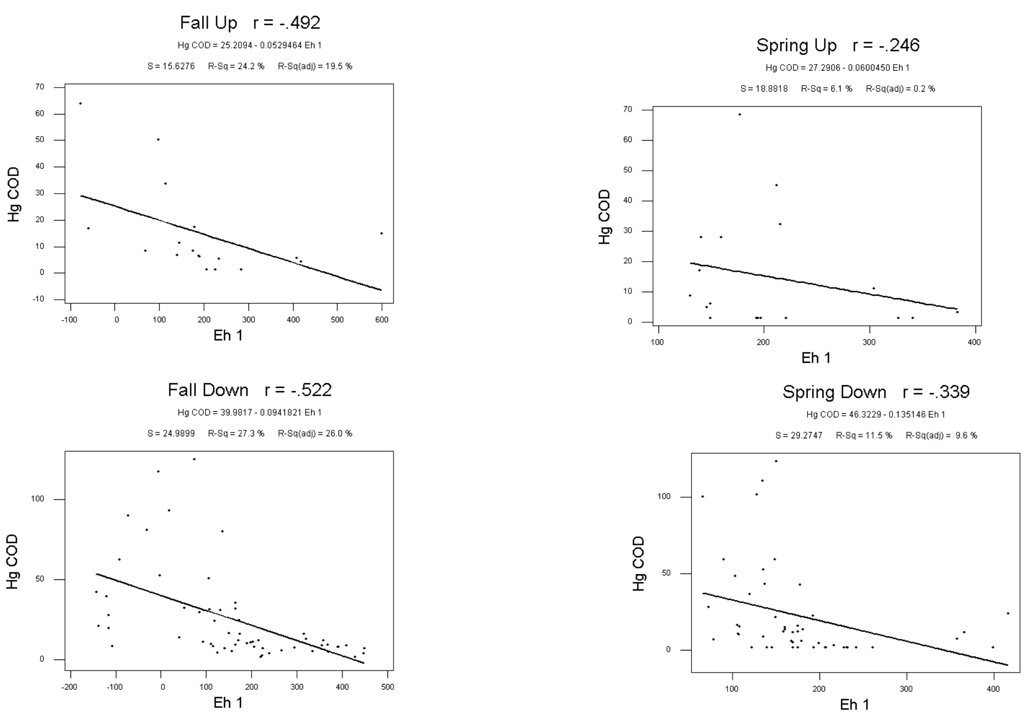


FIGURE 18. CORRELATION OF COD VERSUS DO FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES

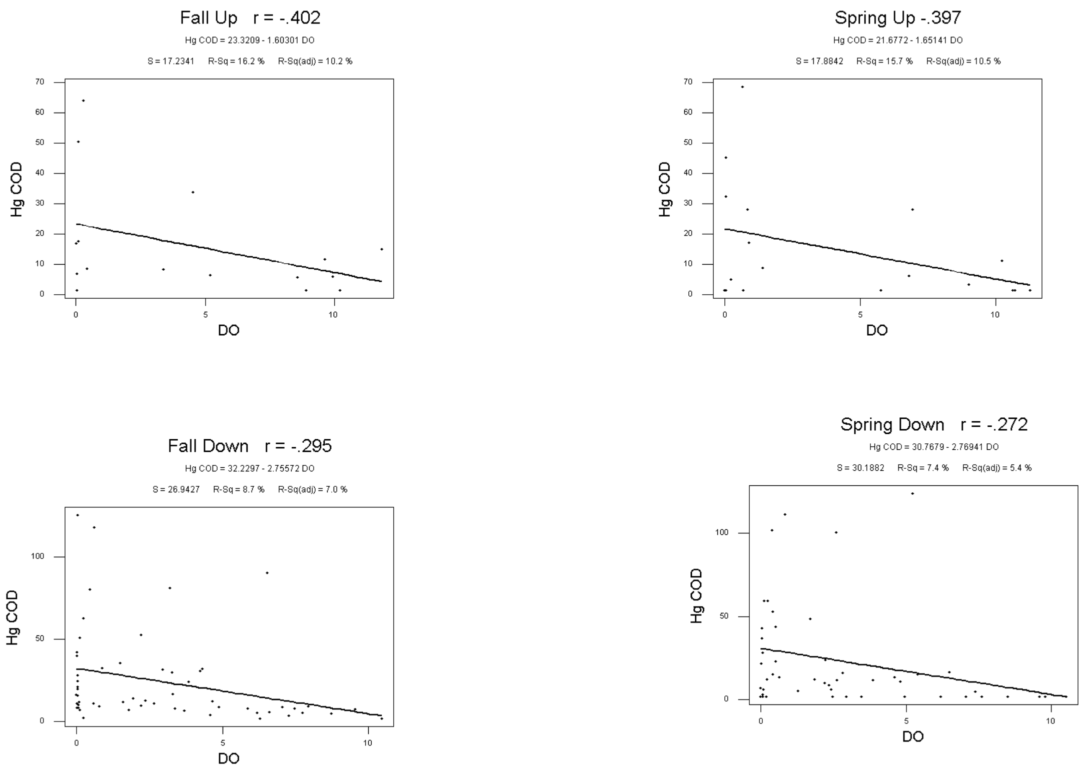



FIGURE 19. CORRELATION OF COD VERSUS CONDUCTIVITY FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES

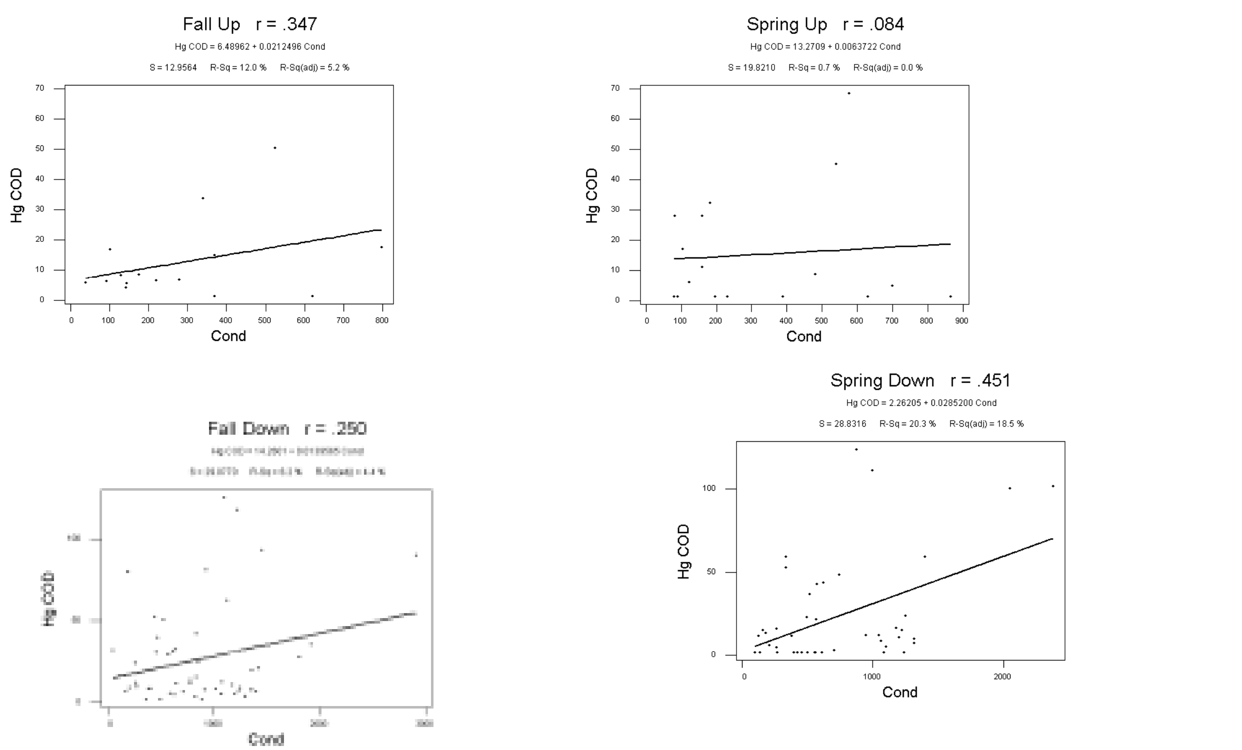


FIGURE 20. CORRELATION OF COD VERSUS AMMONIUM FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES

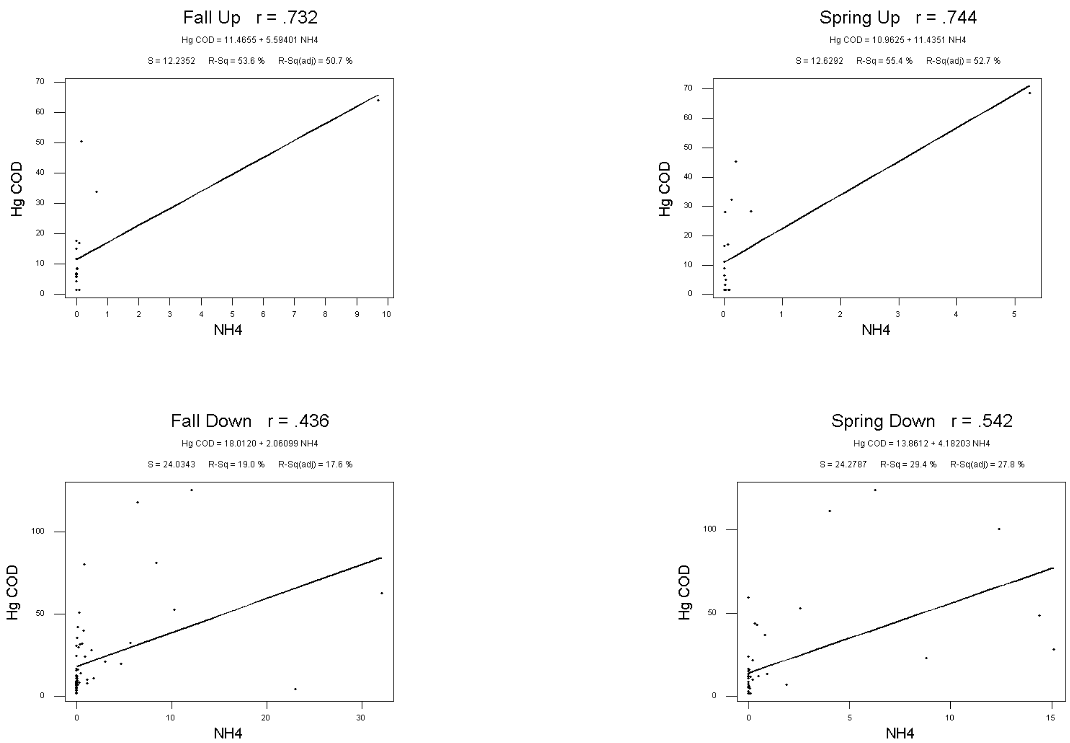



FIGURE 21. CORRELATION OF DOC VERSUS IRON FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

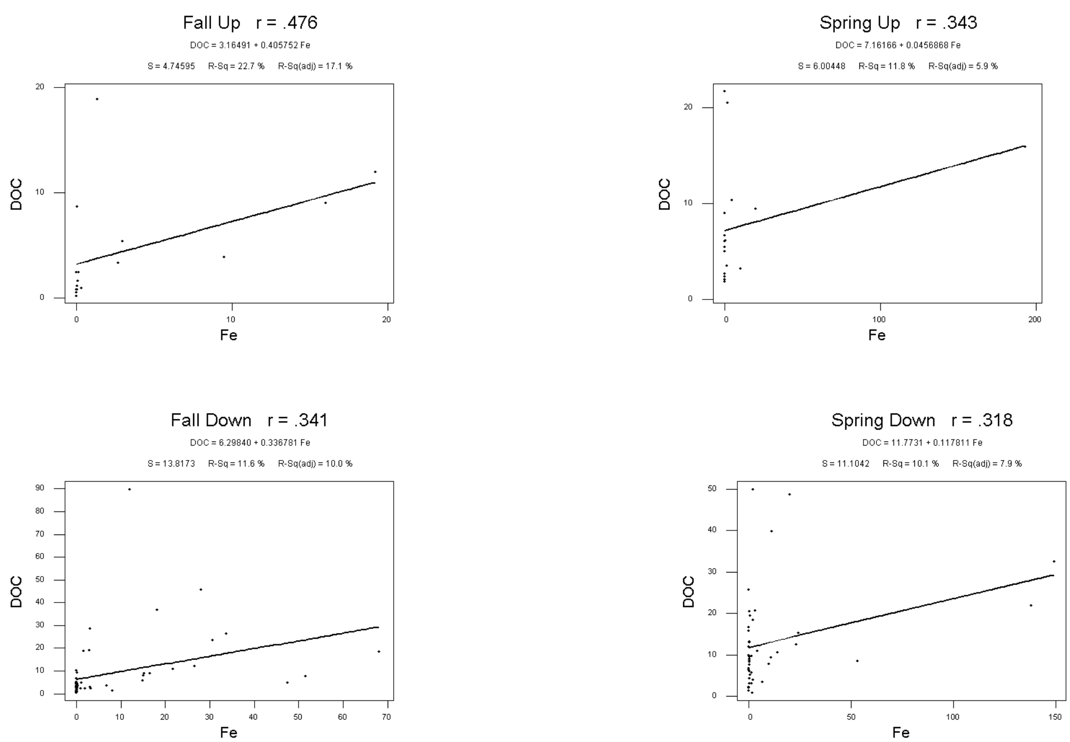


FIGURE 22. CORRELATION OF DOC VERSUS MANGANESE FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

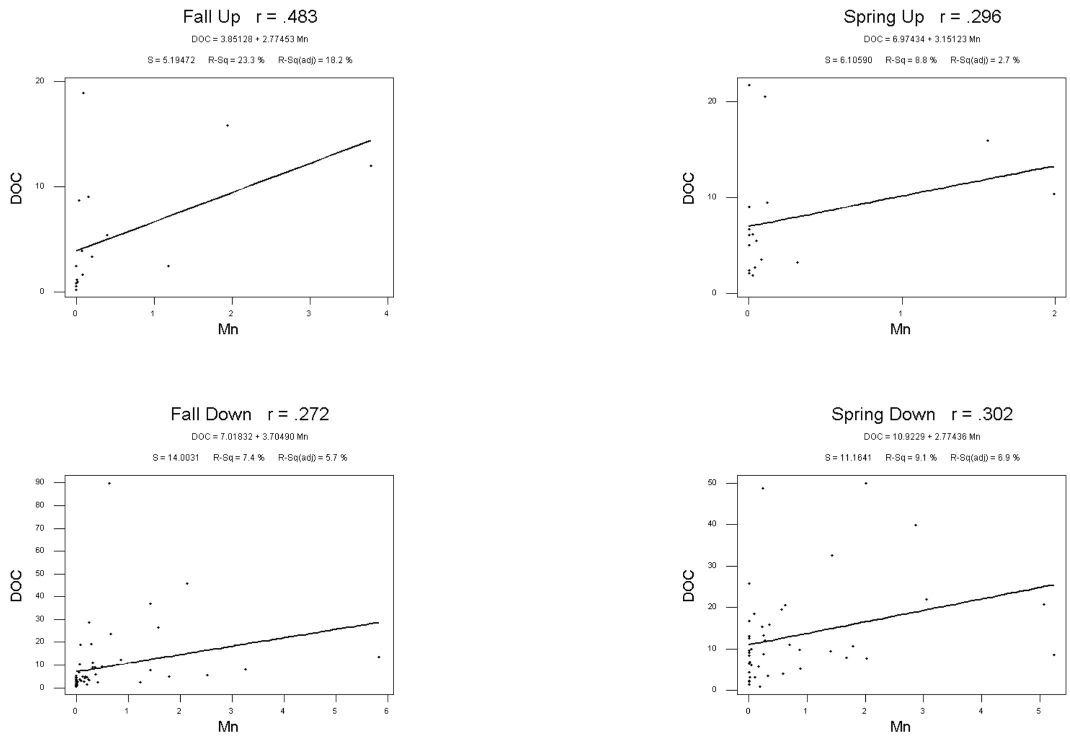



FIGURE 23. CORRELATION OF DOC VERSUS EH FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

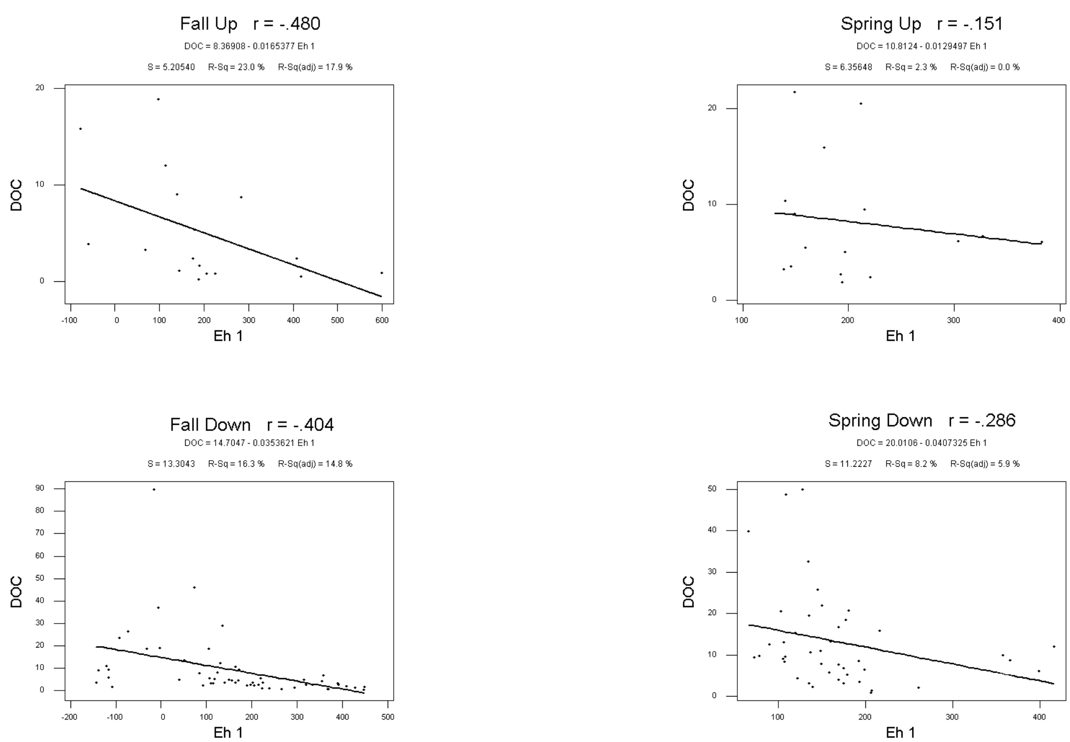


FIGURE 24. CORRELATION OF DOC VERSUS DO FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

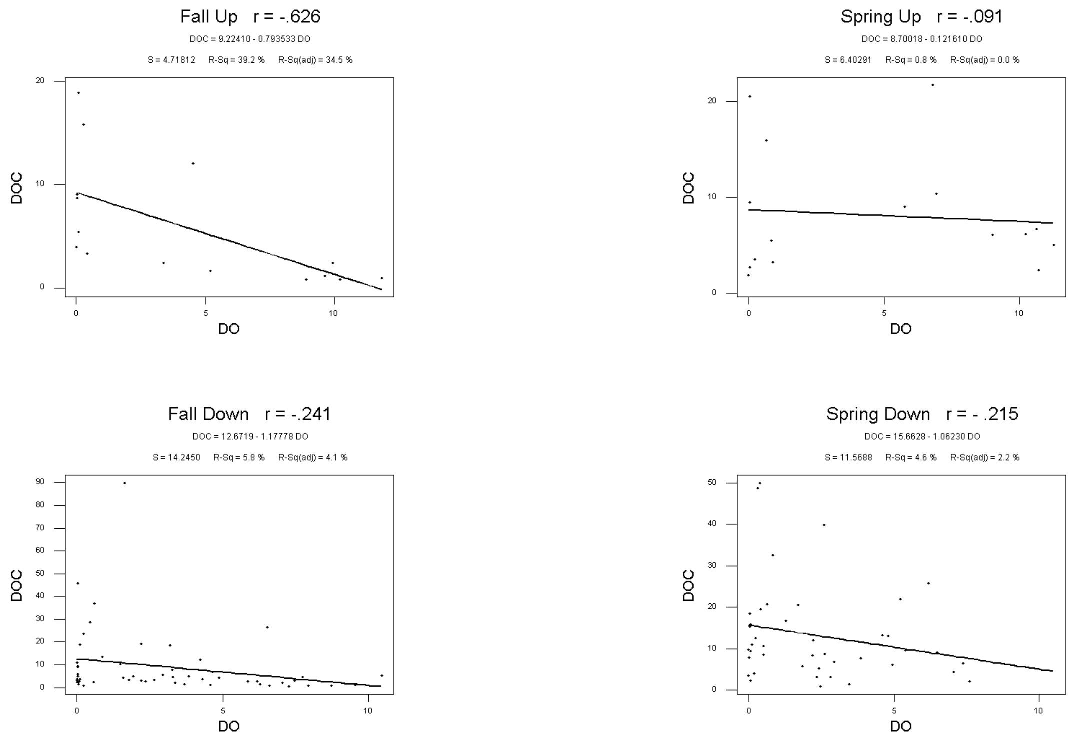



FIGURE 25. CORRELATION OF DOC VERSUS CONDUCTIVITY FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

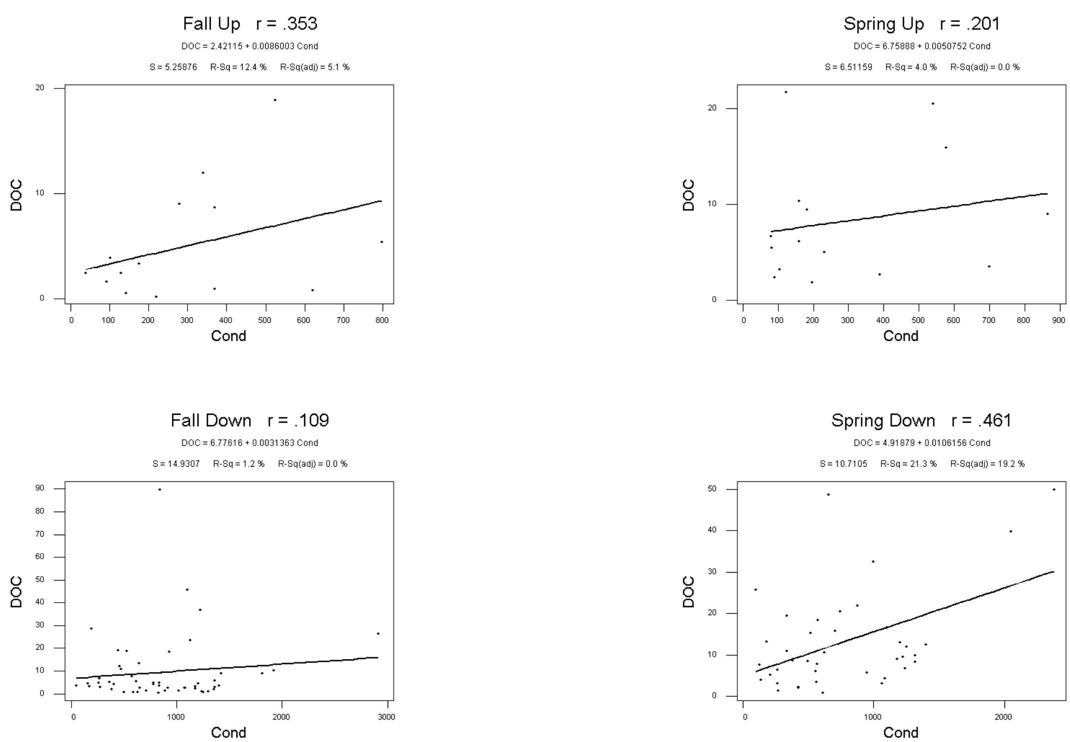


FIGURE 26. CORRELATION OF DOC VERSUS AMMONIUM FOR FALL AND SPRING UPGRADIENT AND DOWNGRADIENT SAMPLES.

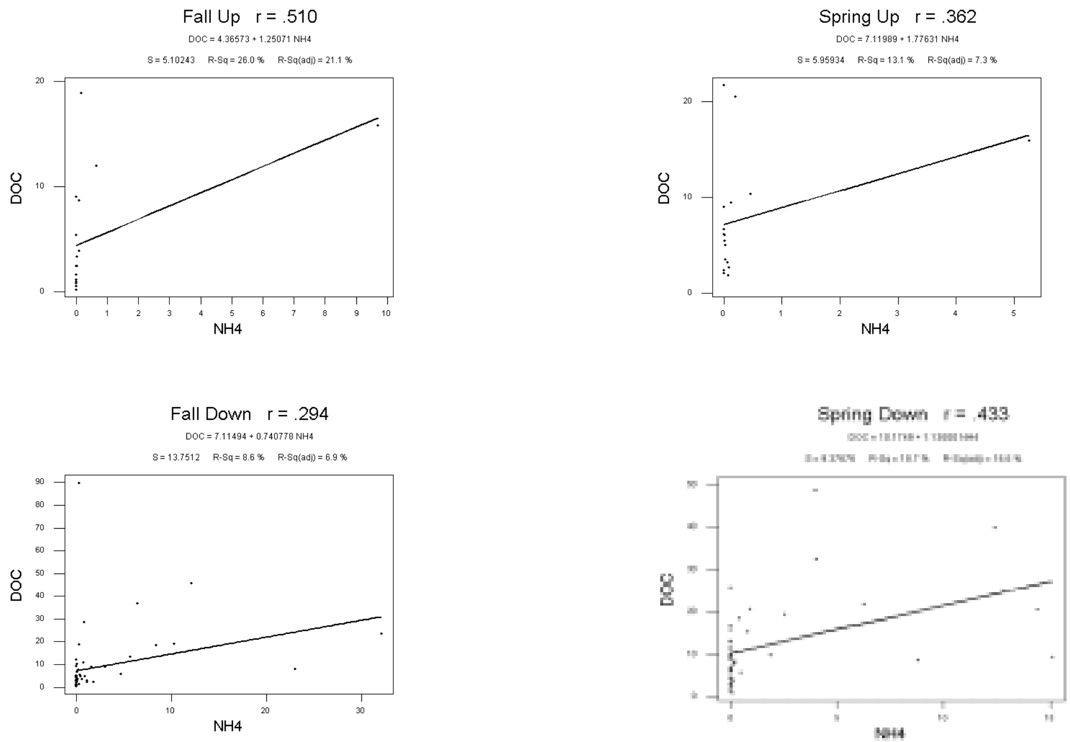


**TABLE 14 Pearson correlation coefficients and p-values for analytical combinations for all data, municipal, and paper mill landfills.**

All Data

| | DO | Cond | Eh 1 | pH | Temp | NH4 | Hg COD | Mn |
|---|---|---|---|---|---|---|---|---|
| Cond | -0.123 | | | | | | | |
| | 0.140 | | | | | | | |
| Eh 1 | 0.461 | -0.242 | | | | | | |
| | 0.000 | 0.003 | | | | | | |
| pH | 0.064 | 0.367 | 0.118 | | | | | |
| | 0.474 | 0.000 | 0.178 | | | | | |
| Temp | 0.024 | 0.343 | -0.174 | 0.212 | | | | |
| | 0.773 | 0.000 | 0.028 | 0.015 | | | | |
| NH4 | -0.197 | 0.258 | -0.376 | -0.151 | 0.098 | | | |
| | 0.015 | 0.002 | 0.000 | 0.089 | 0.228 | | | |
| Hg COD | -0.328 | 0.354 | -0.433 | -0.214 | -0.010 | 0.485 | | |
| | 0.000 | 0.000 | 0.000 | 0.014 | 0.904 | 0.000 | | |
| Mn | -0.219 | 0.067 | -0.279 | -0.282 | -0.061 | 0.400 | 0.387 | |
| | 0.006 | 0.421 | 0.000 | 0.001 | 0.449 | 0.000 | 0.000 | |
| Fe | -0.153 | 0.145 | -0.246 | -0.209 | -0.076 | 0.325 | 0.600 | 0.381 |
| | 0.059 | 0.080 | 0.002 | 0.016 | 0.347 | 0.000 | 0.000 | 0.000 |
| DOC | -0.285 | 0.256 | -0.333 | -0.042 | -0.152 | 0.316 | 0.810 | 0.280 |
| | 0.001 | 0.003 | 0.000 | 0.648 | 0.068 | 0.000 | 0.000 | 0.001 |
| Mn COD | 0.008 | -0.085 | 0.115 | 0.025 | 0.061 | -0.357 | -0.326 | -0.196 |
| | 0.984 | 0.827 | 0.768 | 0.950 | 0.876 | 0.432 | 0.529 | 0.613 |

| | Fe | DOC |
|---|---|---|
| DOC | 0.307 | |
| | 0.000 | |
| Mn COD | 0.126 | -0.313 |
| | 0.746 | 0.450 |

Municipal

| | DO | Cond | Eh 1 | NH4 | Hg COD | Mn | Fe | DOC |
|---|---|---|---|---|---|---|---|---|
| Cond | -0.085 | | | | | | | |
| | 0.408 | | | | | | | |
| Eh 1 | 0.438 | -0.272 | | | | | | |
| | 0.000 | 0.007 | | | | | | |
| NH4 | -0.199 | 0.182 | -0.259 | | | | | |
| | 0.042 | 0.077 | 0.007 | | | | | |
| Hg COD | -0.311 | 0.279 | -0.364 | 0.229 | | | | |
| | 0.001 | 0.006 | 0.000 | 0.018 | | | | |
| Mn | -0.219 | 0.021 | -0.190 | 0.528 | 0.134 | | | |
| | 0.023 | 0.840 | 0.048 | 0.000 | 0.170 | | | |
| Fe | -0.207 | 0.269 | -0.323 | 0.584 | 0.698 | 0.288 | | |
| | 0.033 | 0.008 | 0.001 | 0.000 | 0.000 | 0.002 | | |
| DOC | -0.249 | 0.070 | -0.295 | 0.074 | 0.681 | 0.147 | 0.364 | |
| | 0.013 | 0.516 | 0.003 | 0.466 | 0.000 | 0.144 | 0.000 | |
| Mn COD | -0.506 | 0.920 | 0.159 | 0.839 | * | -0.174 | 0.107 | -0.794 |
| | 0.494 | 0.080 | 0.841 | 0.366 | * | 0.826 | 0.893 | 0.416 |

* NOTE * Not enough data in column.

**Paper Mill**

| | DO | Cond | Eh 1 | NH4 | Hg COD | Mn | Fe | DOC |
|---|---|---|---|---|---|---|---|---|
| Cond | -0.333 | | | | | | | |
| | 0.022 | | | | | | | |
| Eh 1 | 0.510 | -0.230 | | | | | | |
| | 0.000 | 0.109 | | | | | | |
| NH4 | -0.223 | 0.537 | -0.508 | | | | | |
| | 0.137 | 0.000 | 0.000 | | | | | |
| Hg COD | -0.356 | 0.663 | -0.532 | 0.562 | | | | |
| | 0.013 | 0.000 | 0.000 | 0.000 | | | | |
| Mn | -0.122 | 0.310 | -0.402 | 0.217 | 0.494 | | | |
| | 0.410 | 0.029 | 0.003 | 0.134 | 0.000 | | | |
| Fe | -0.100 | 0.180 | -0.224 | 0.229 | 0.519 | 0.378 | | |
| | 0.508 | 0.215 | 0.122 | 0.121 | 0.000 | 0.007 | | |
| DOC | -0.328 | 0.739 | -0.393 | 0.611 | 0.895 | 0.456 | 0.275 | |
| | 0.028 | 0.000 | 0.006 | 0.000 | 0.000 | 0.001 | 0.065 | |
| Mn COD | 0.689 | -0.845 | 0.490 | -0.512 | 0.825 | 0.380 | 0.743 | -0.840 |
| | 0.198 | 0.071 | 0.402 | 0.488 | 0.085 | 0.529 | 0.150 | 0.075 |

**TABLE 15. Pearson correlation coefficients and p-values for analytical combinations for fall and spring upgradient and downgradient samples.**

**FallUp**

| | DO | Cond | Eh 1 | NH4 | Hg COD | Mn | Fe |
|---|---|---|---|---|---|---|---|
| Cond | -0.170 | | | | | | |
| | 0.579 | | | | | | |
| Eh 1 | 0.666 | -0.021 | | | | | |
| | 0.005 | 0.941 | | | | | |
| NH4 | -0.260 | 0.112 | -0.436 | | | | |
| | 0.330 | 0.690 | 0.071 | | | | |
| Hg COD | -0.402 | 0.347 | -0.492 | 0.732 | | | |
| | 0.122 | 0.206 | 0.038 | 0.001 | | | |
| Mn | -0.196 | 0.055 | -0.346 | 0.438 | 0.553 | | |
| | 0.467 | 0.844 | 0.160 | 0.069 | 0.017 | | |
| Fe | -0.397 | 0.025 | -0.427 | 0.685 | 0.365 | 0.666 | |
| | 0.143 | 0.930 | 0.088 | 0.002 | 0.150 | 0.004 | |
| DOC | -0.626 | 0.353 | -0.480 | 0.510 | 0.834 | 0.483 | 0.476 |
| | 0.013 | 0.216 | 0.051 | 0.036 | 0.000 | 0.049 | 0.062 |

Spring Up

| | DO | Cond | Eh 1 | NH4 | Hg COD | Mn | Fe |
|---|---|---|---|---|---|---|---|
| Cond | -0.397 | | | | | | |
| | 0.115 | | | | | | |
| Eh 1 | 0.391 | -0.112 | | | | | |
| | 0.109 | 0.670 | | | | | |
| NH4 | -0.208 | 0.243 | -0.130 | | | | |
| | 0.409 | 0.348 | 0.607 | | | | |
| Hg COD | -0.397 | 0.084 | -0.246 | 0.744 | | | |
| | 0.103 | 0.749 | 0.325 | 0.000 | | | |
| Mn | -0.123 | 0.060 | -0.380 | 0.596 | 0.575 | | |
| | 0.628 | 0.820 | 0.120 | 0.007 | 0.010 | | |
| Fe | -0.231 | 0.227 | -0.123 | 0.993 | 0.745 | 0.550 | |
| | 0.356 | 0.382 | 0.628 | 0.000 | 0.000 | 0.015 | |
| DOC | -0.091 | 0.201 | -0.151 | 0.362 | 0.550 | 0.296 | 0.343 |
| | 0.736 | 0.473 | 0.578 | 0.153 | 0.022 | 0.248 | 0.177 |

Fall Down

| | DO | Cond | Eh 1 | NH4 | Hg COD | Mn | Fe | DOC |
|---|---|---|---|---|---|---|---|---|
| Cond | 0.045 | | | | | | | |
| | 0.745 | | | | | | | |
| Eh 1 | 0.580 | -0.219 | | | | | | |
| | 0.000 | 0.109 | | | | | | |
| NH4 | -0.229 | 0.153 | -0.361 | | | | | |
| | 0.089 | 0.273 | 0.006 | | | | | |
| Hg COD | -0.295 | 0.250 | -0.522 | 0.436 | | | | |
| | 0.027 | 0.068 | 0.000 | 0.001 | | | | |
| Mn | -0.242 | -0.038 | -0.328 | 0.373 | 0.383 | | | |
| | 0.073 | 0.785 | 0.012 | 0.004 | 0.003 | | | |
| Fe | -0.116 | 0.158 | -0.522 | 0.411 | 0.559 | 0.628 | | |
| | 0.399 | 0.258 | 0.000 | 0.002 | 0.000 | 0.000 | | |
| DOC | -0.241 | 0.109 | -0.404 | 0.294 | 0.953 | 0.272 | 0.341 | |
| | 0.076 | 0.441 | 0.002 | 0.028 | 0.000 | 0.042 | 0.011 | |
| Mn COD | 1.000 | -1.000 | -1.000 | -1.000 | * | -1.000 | -1.000 | 1.000 |
| | * | * | * | * | * | * | * | * |

* NOTE * Not enough data in column.

**Spring Down**

| | DO | Cond | Eh 1 | NH4 | Hg COD | Mn | Fe | DOC |
|---|---|---|---|---|---|---|---|---|
| Cond | -0.173 | | | | | | | |
| | 0.250 | | | | | | | |
| Eh 1 | 0.311 | -0.252 | | | | | | |
| | 0.028 | 0.088 | | | | | | |
| NH4 | -0.210 | 0.294 | -0.368 | | | | | |
| | 0.156 | 0.053 | 0.010 | | | | | |
| Hg COD | -0.272 | 0.451 | -0.339 | 0.542 | | | | |
| | 0.061 | 0.002 | 0.017 | 0.000 | | | | |
| Mn | -0.263 | 0.091 | -0.151 | 0.472 | 0.442 | | | |
| | 0.065 | 0.541 | 0.289 | 0.001 | 0.001 | | | |
| Fe | -0.103 | 0.112 | -0.159 | 0.322 | 0.684 | 0.411 | | |
| | 0.478 | 0.452 | 0.266 | 0.026 | 0.000 | 0.003 | | |
| DOC | -0.215 | 0.461 | -0.286 | 0.433 | 0.760 | 0.302 | 0.318 | |
| | 0.172 | 0.003 | 0.063 | 0.005 | 0.000 | 0.049 | 0.038 | |
| Mn COD | -0.036 | -0.113 | 0.107 | -0.345 | -0.331 | -0.211 | 0.103 | -0.760 |
| | 0.939 | 0.809 | 0.819 | 0.570 | 0.586 | 0.650 | 0.826 | 0.079 |

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## Appendix 1: Additional Case Studies

Note: When the text refers to figures in this appendix, the reference omits the A1 that precedes each figure number.

## Flambeau Paper Landfill

Even though many sites have the *COD Effective / Other Parameter Effective* combination, the data were not always clearly showing increasing contamination with time. The Flambeau Paper landfill is an example of this. Data for the Flambeau Paper landfill show high levels at the start of monitoring but decreasing concentration with time. However, the down gradient wells were clearly impacted and contamination was prevalent.

Ammonia Nitrogen and Nitrate+Nitrite were not tested at this landfill, despite being two parameters currently required for paper mill sludge landfills. Each parameter is showing an overall impact between up gradient well FOW-6 and down gradient wells. To receive a yes response, the parameters needed only to show an overall impact, regardless of the trend seen.

Figures 1A - 1F1 show the time versus concentration graphs for required indicator parameters. Note that not all the same wells were selected for every parameter. Wells for each parameter were selected based on those wells indicating the most contamination in non-parametric box plots. Alkalinity data are plotted in Figures 1A and 1A1. Figure 1a1 contains the same data as Figure 1a but omits the outlier point #13. Alkalinity concentration is still very high and remains elevated, even at later dates. Figure 1b is the time versus concentration graph of chloride data. Chloride has a standard PAL of 125 mg/l, and this value is also plotted on the graph. A similar decreasing trend among most of the parameters is also seen for chloride. However, the extent of contamination is easier to see by comparing the data to the PAL. Figure 1C and 1C1 show COD data. Without Well #1, levels of COD are still extremely high and impacts in down gradient wells are clear. Conductivity and hardness data are shown in Figure 1D and Figure 1E. Both conductivity and hardness have similar trends and have very high concentration readings. Finally, Figure 1F and Figure 1F1 show sulfate data. Sulfate is not showing the same trends as other parameters, but with knowing the PAL, impacts are obvious.

The summary sheet for Flambeau Paper landfill is shown in Appendix 2. All parameters monitored indicate an overall impact between up gradient and down gradient wells. The main indicator parameters also show the same decreasing trend. The wells selected for each parameter, though not exactly the same, were very similar. Leachate data was somewhat helpful in showing overall impacts. Also, either no PAL/ACL exceedances for VOCs were found or no VOCs were tested at the Flambeau Paper landfill. The fact that the levels were extremely high for all of the parameters was a key factor in this case, and thus, the decision to drop COD was made because the contamination would have been clearly detected without COD.

FIGURE A1 - 1A: TIME VS. CONCENTRATION GRAPH OF ALKALINITY DATA FOR FLAMBEAU PAPER LANDFILL

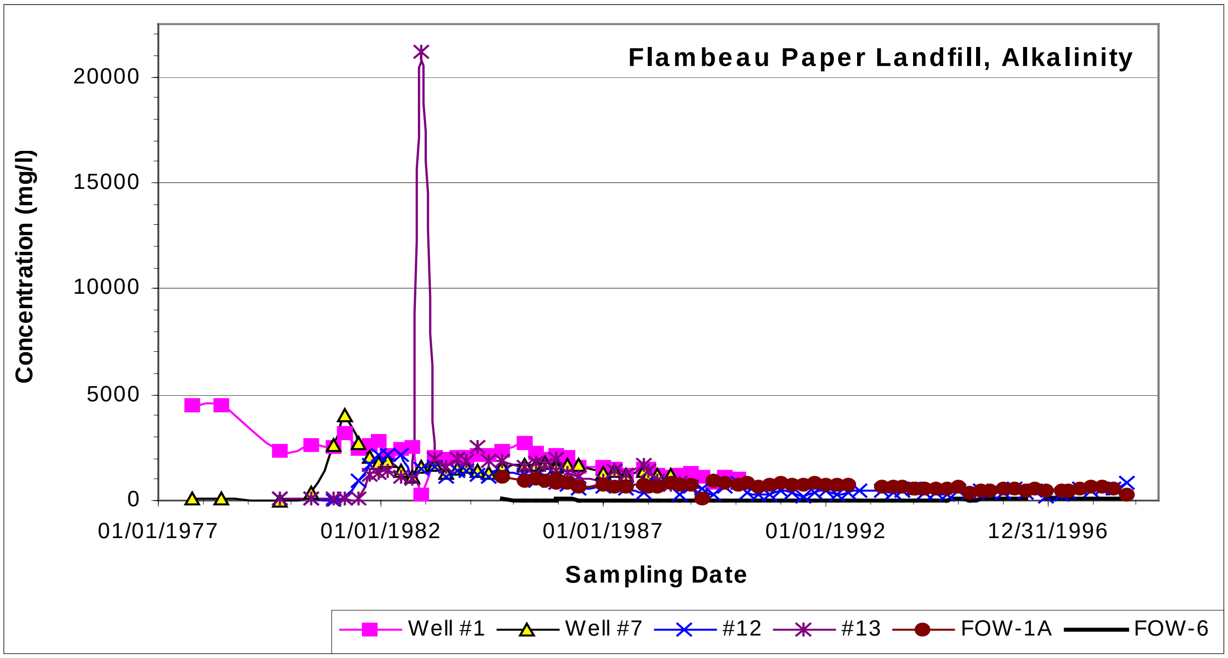



FIGURE A1 - 1A1: TIME VS. CONCENTRATION GRAPH OF ALKALINITY DATA FOR FLAMBEAU PAPER LANDFILL, WITHOUT #13.

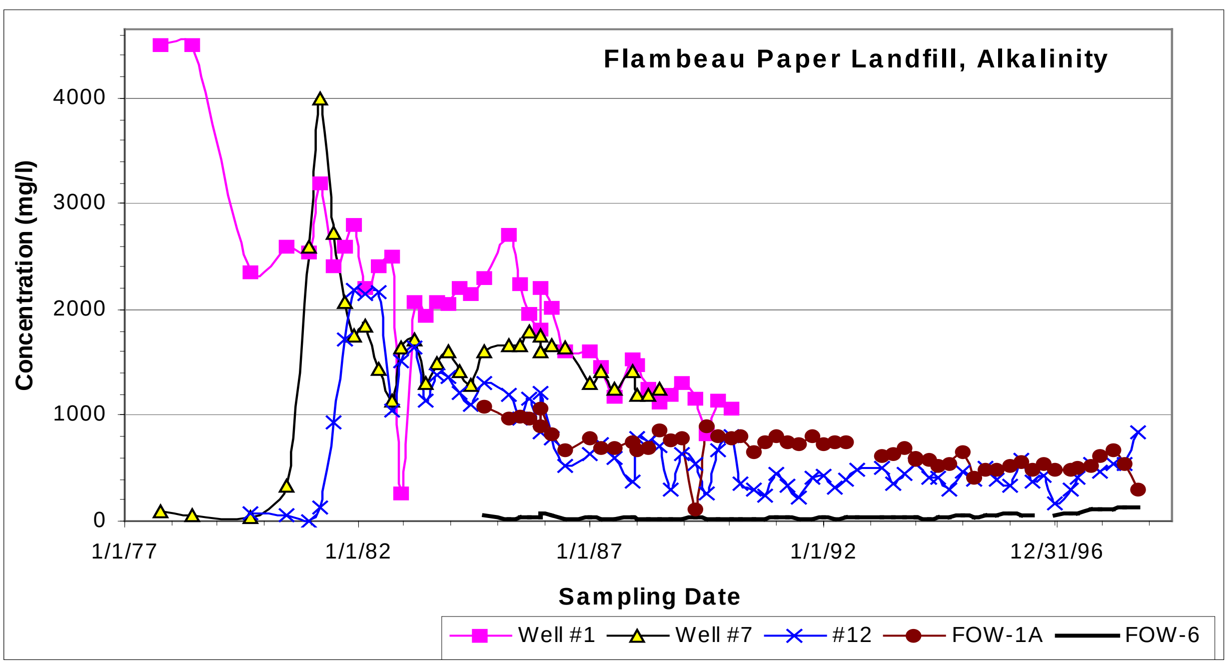


FIGURE A1 - 1B: TIME VS. CONCENTRATION GRAPH OF CHLORIDE DATA FOR FLAMBEAU PAPER LANDFILL.

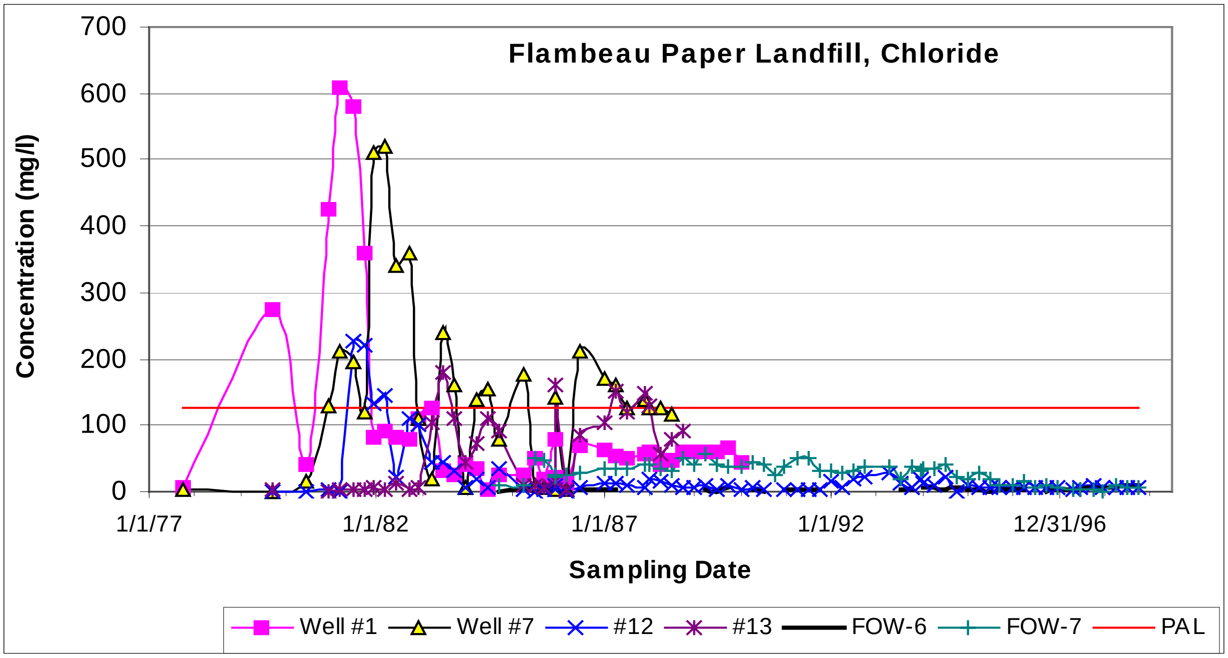



FIGURE A1 - 1C: TIME VS. CONCENTRATION GRAPH OF COD DATA FOR FLAMBEAU PAPER LANDFILL.

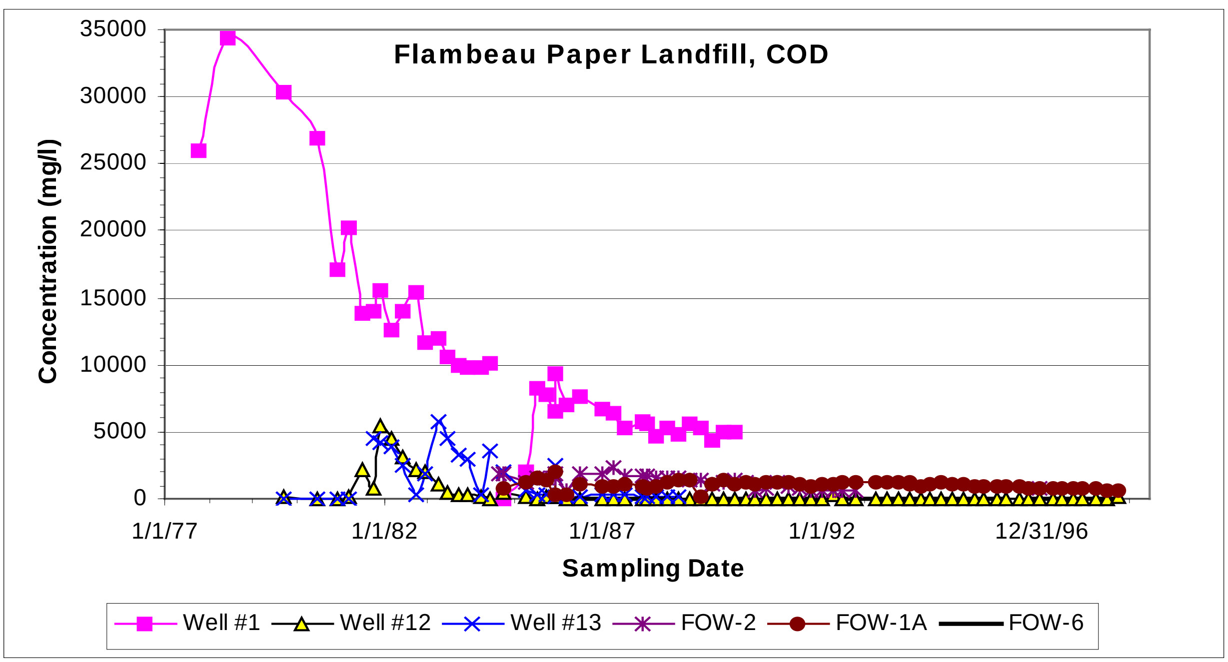


FIGURE A1 - 1C1: TIME VS. CONCENTRATION GRAPH OF COD DATA FOR FLAMBEAU PAPER LANDFILL, WITHOUT WELL #1.

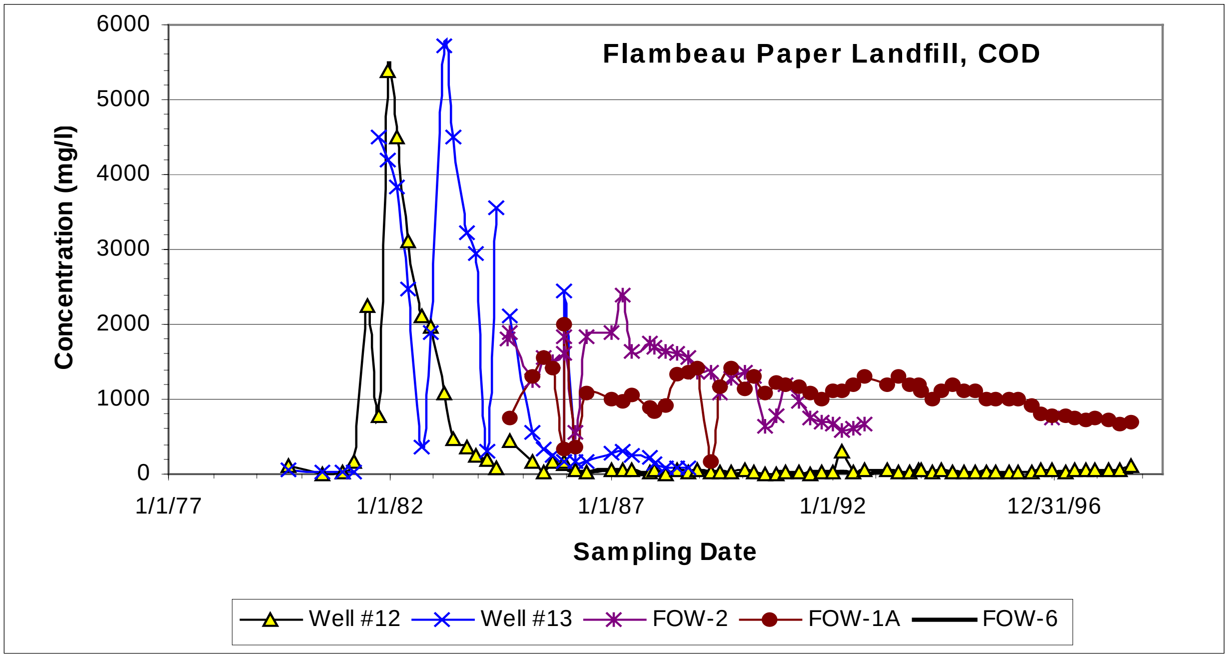



FIGURE A1 - 1D: TIME VS. CONCENTRATION GRAPH OF CONDUCTIVITY DATA FOR FLAMBEAU PAPER LANDFILL.

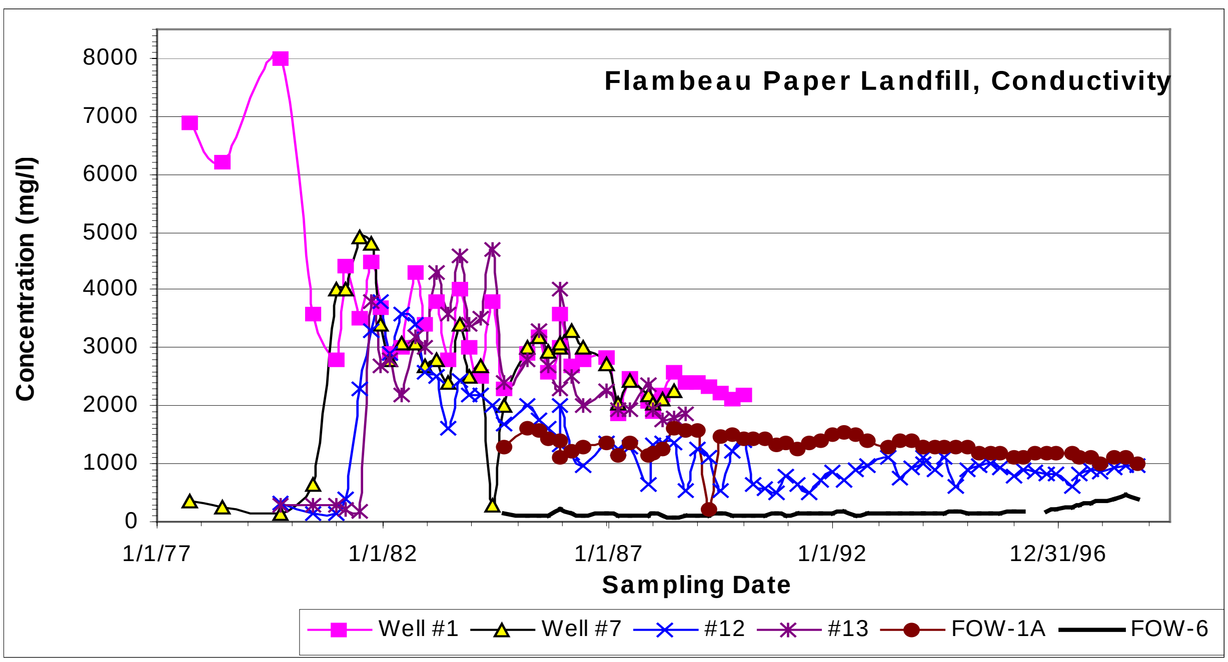


FIGURE A1 - 1E: TIME VS. CONCENTRATION GRAPH OF HARDNESS DATA FOR FLAMBEAU PAPER LANDFILL.

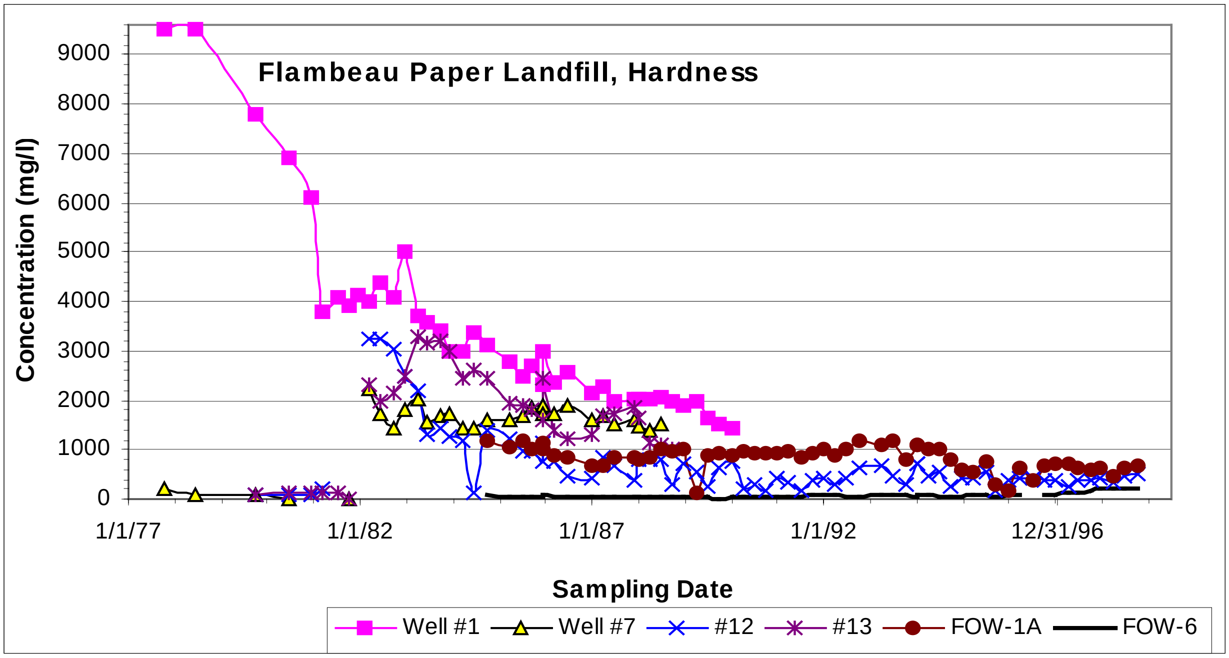



FIGURE A1 - 1F: TIME VS. CONCENTRATION GRAPH OF SULFATE DATA FOR FLAMBEAU PAPER LANDFILL.

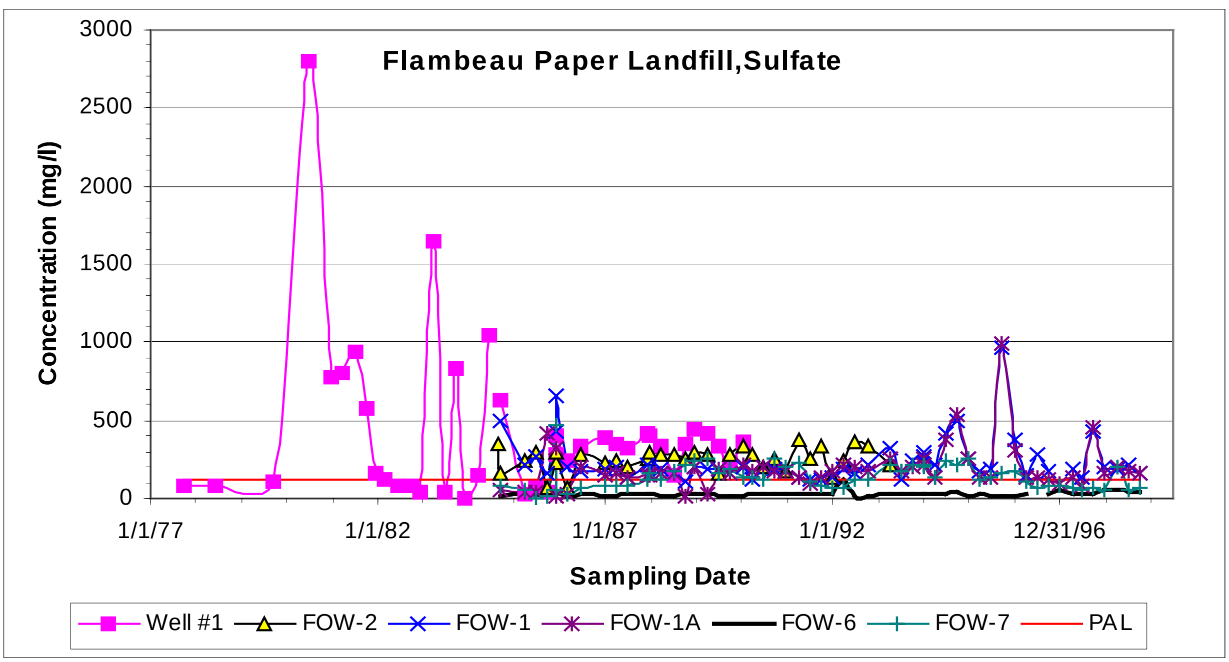
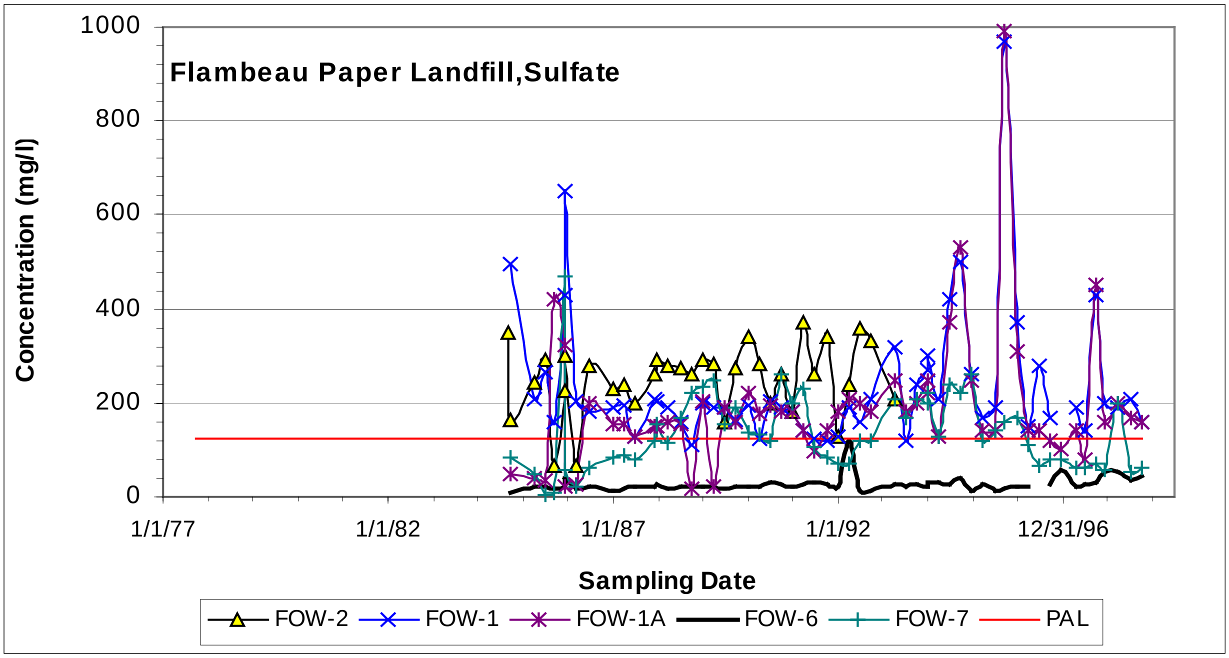


FIGURE A1 - 1F1: TIME VS. CONCENTRATION GRAPH OF SULFATE DATA FOR FLAMBEAU PAPER LANDFILL, WITHOUT WELL #1



## Oconto Falls Landfill

The Oconto Falls Landfill was the only case where COD was a useful parameter, and without it, contamination would not have been caught as early as it was (*COD Effective / Other Parameters Not Effective*). The City of Oconto Falls Landfill was selected for this study because it was specifically mentioned in the COD survey (April 1998) as a site where COD was used to take remedial action. Survey respondents also cited hardness and pH as parameters used to prove groundwater standards had been violated.

Landfilling at the Oconto Falls Landfill began in 1967 in a small ravine, approximately 30 feet deep. The landfill site was a former gravel pit and groundwater flowed through the waste from the southwest to the northeast. In 1970, the landfill was officially licensed. The location of the landfill was within 160 ft of Dump Creek, a class I trout stream, which flowed along the western and northern boundaries of the site. Additionally, a wetland area was located approximately 200 feet east of the landfill. Open burning occurred at the site in the late 1970s to early 1980s, and in 1981 a major leachate seep flowing into Dump Creek was discovered.

Monitoring wells were installed in 1982 after the DNR asked for a plan of mitigation. In 1985, cedar trees down gradient from the landfill were dying and the City illegally filled in the wetland. The DNR requested a remedial action or closure plan. In 1986, the DNR required that extraction wells downgradient from the landfill be installed. The City delayed on closure plans, so in 1987, the DNR issued a proposed order to close the landfill. In May 1988, the City of Oconto Falls signed a consent order to close the landfill and by February 1990, final leachate and groundwater extraction systems began operating. In 1991, the landfill was officially closed with a NR 180 cap, passive gas venting system, and springwater diversion system. The City of Oconto Falls was also to pay fines and restore Dump Creek.

Looking at box plots, wells were selected for time versus concentration graphs which are shown in Figures 2A-F. Figure 2a shows alkalinity data. A preventative action limit (PAL) of 1230 was established for this site and as seen in Figure 2A, only well B-12A exceeds that value more than once. However, an overall impact is seen between upgradient well B-1 and the other wells, which is an indication of contamination despite the low levels compared to the PAL.

Chloride data, shown in Figure 2B, appears to be decreasing. Chloride always has a PAL of 125 and an enforcement standard (ES) of 250. Comparing the data to the background levels from B-1, an overall impact is seen, but again, the levels are not significantly high when using the PAL and the ES.

Figure 2C contains data for COD, and at first glance, the data appears to be somewhat confusing. However, a PAL of 38 was established for the site, which makes a big difference because all of the downgradient wells exceed this value substantially. B-1 also exceeded the PAL, but the exceedance appears to be an outlier.

Conductivity data, shown in Figure 2D, are the best indication of overall contamination at this site. A value of 570 was listed for the PAL and all wells except the background well B-1 exceed the PAL. Also, the separation between B-1 and the other wells is clearly seen. However, when viewing the data more closely, many of the wells show a confusing trend of first decreasing and then increasing.

The other parameters used to take action at the Oconto Falls Landfill where pH and hardness, which data are shown in Figures 2E and 2F. Usually pH data does not show much, but at this site a clear overall change between background well B-1 and the down gradient wells was seen. Additionally, usually pH in downgradient wells or leachate has a higher value than the established background levels. In this case, the opposite occurred, and the background level from B-1 seems quite high. A PAL of 400 was calculated for hardness at this site and in Figure 2f, the data show the contamination clearly with overall impacts and a large increase in B-18.

The Oconto Falls Landfill is an example where COD was used as a good indicator and not all other parameters were showing clear signs of contamination, especially when PAL values were considered. In this case, without COD, there may have been problems showing that groundwater standards had been violated and that action was necessary. However, groundwater monitoring data available are from after contamination had already been discovered at the site so the unclear data may be a result of late testing. Additionally, VOC data, if sampled earlier, most likely would have caught the contamination even more effectively than the indicator parameters in this case.

FIGURE A1 - 2A: TIME VS. CONCENTRATION GRAPH OF ALKALINITY DATA FOR THE OCONTO FALLS LANDFILL.

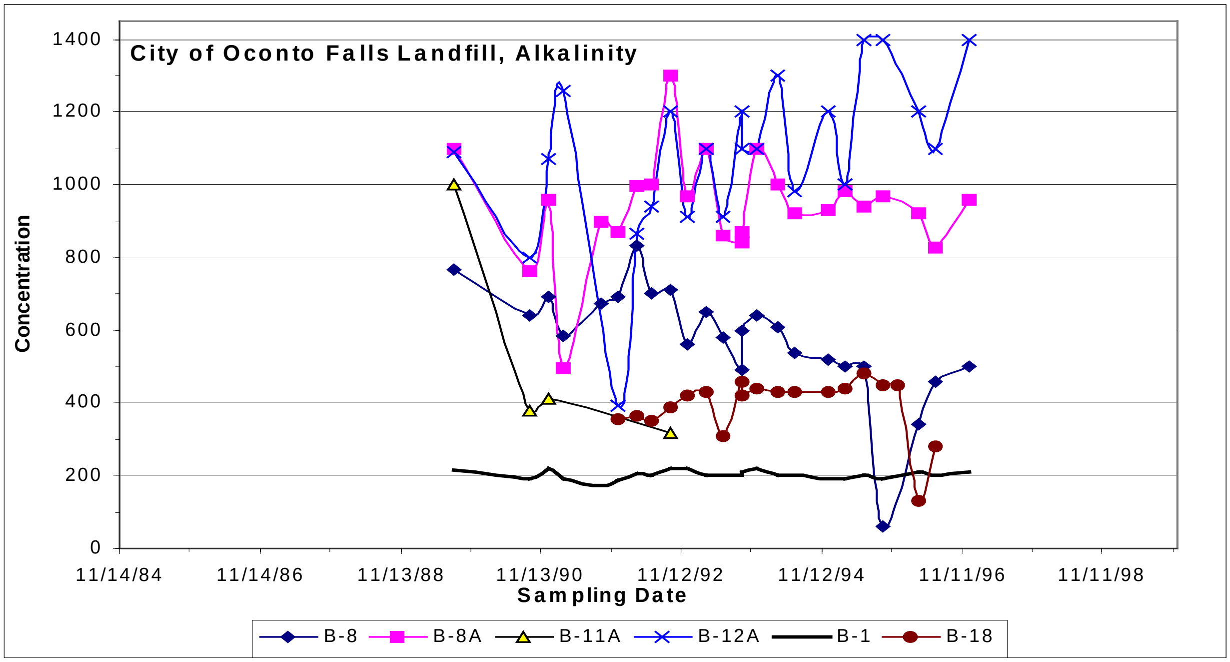



FIGURE A1 - 2B: TIME VS. CONCENTRATION GRAPH OF CHLORIDE DATA FOR THE OCONTO FALLS LANDFILL.

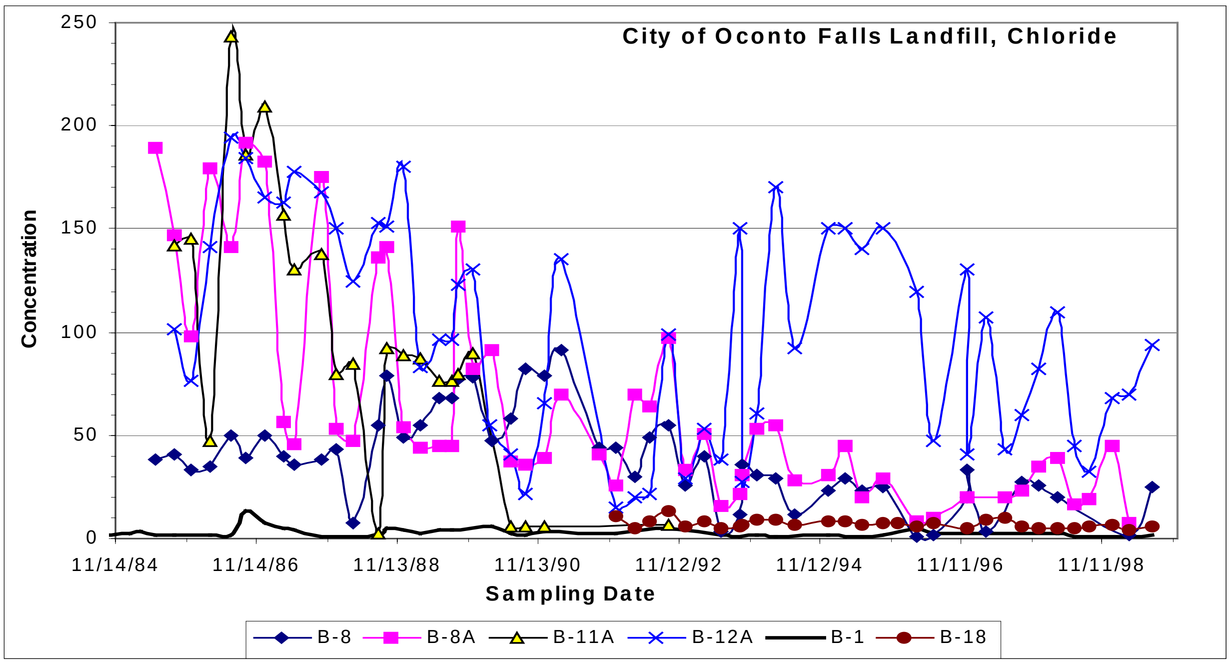


FIGURE A1 - 2C: TIME VS. CONCENTRATION GRAPH OF COD DATA FOR THE OCONTO FALLS LANDFILL.

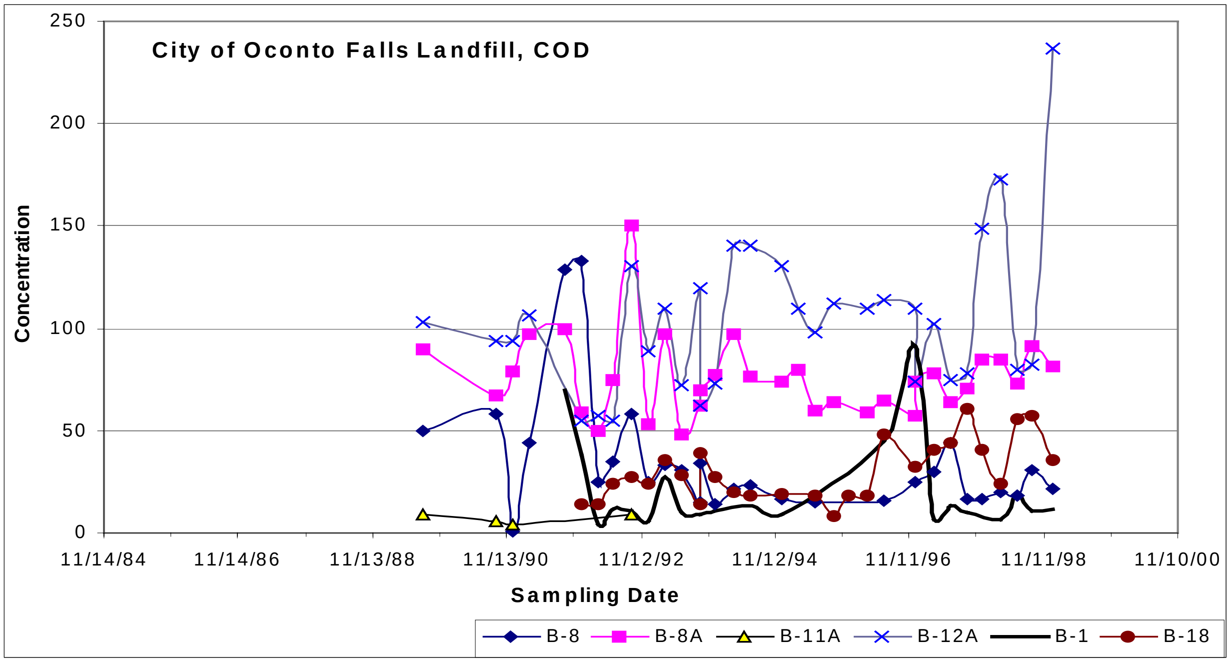



FIGURE A1 - 2D: TIME VS. CONCENTRATION GRAPH OF CONDUCTIVITY DATA FOR THE OCONTO FALLS LANDFILL.

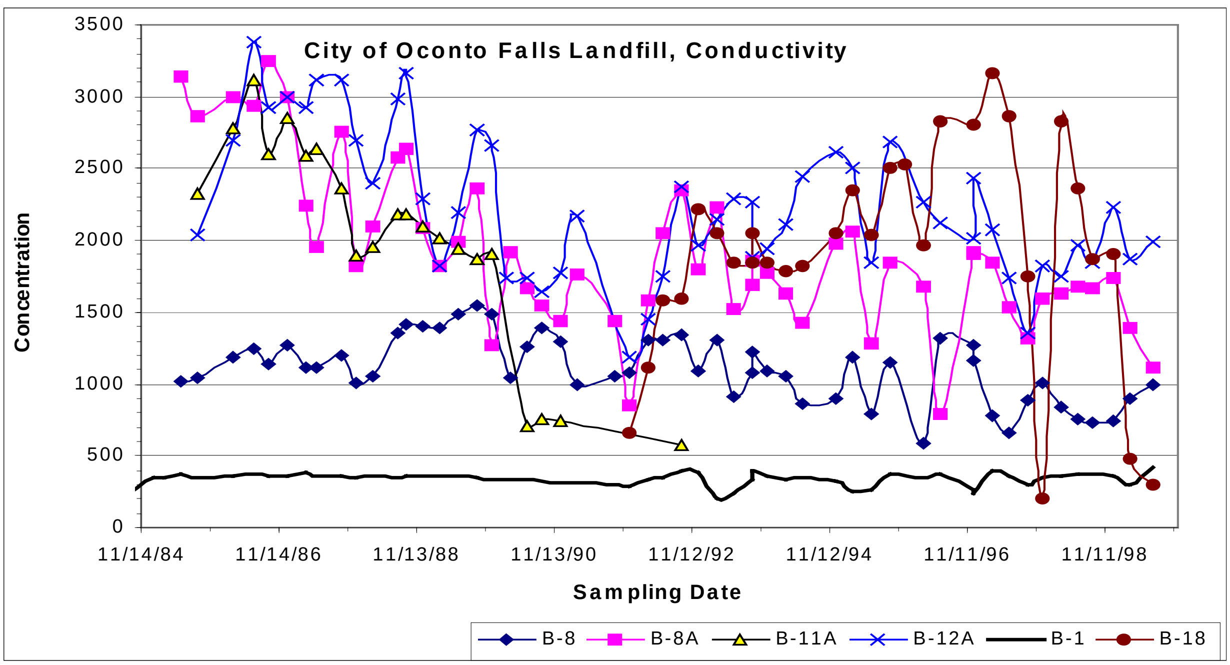


FIGURE A1 - 2E: TIME VS. CONCENTRATION GRAPH OF pH DATA FOR THE OCONTO FALLS LANDFILL.

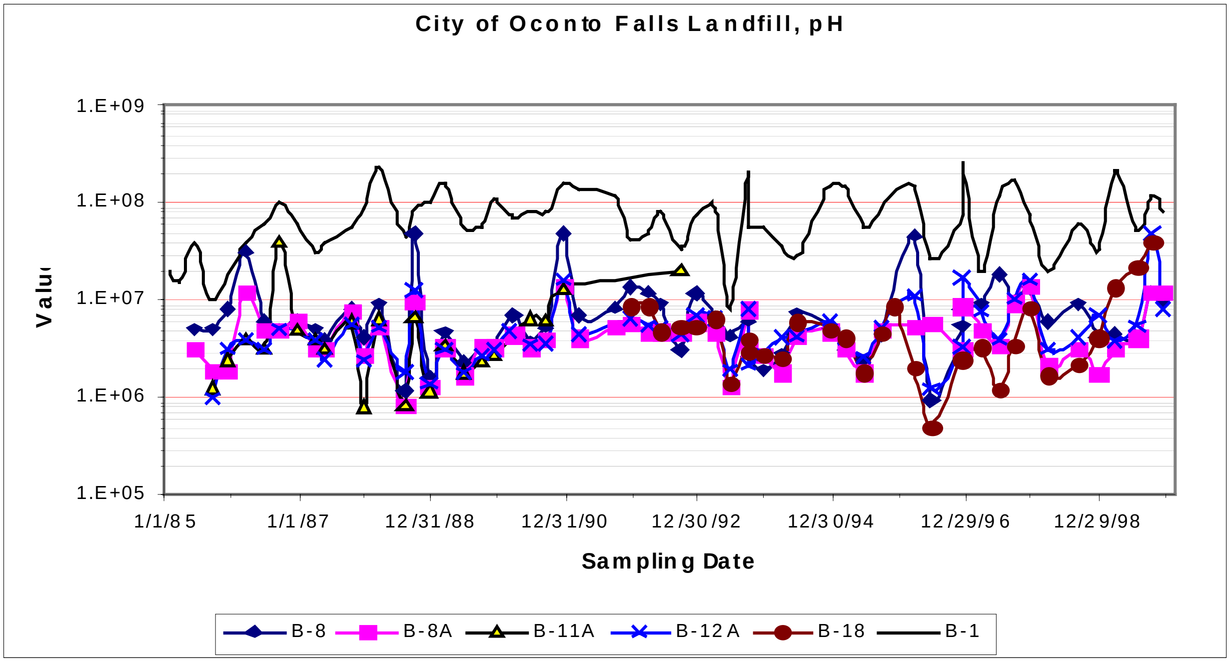
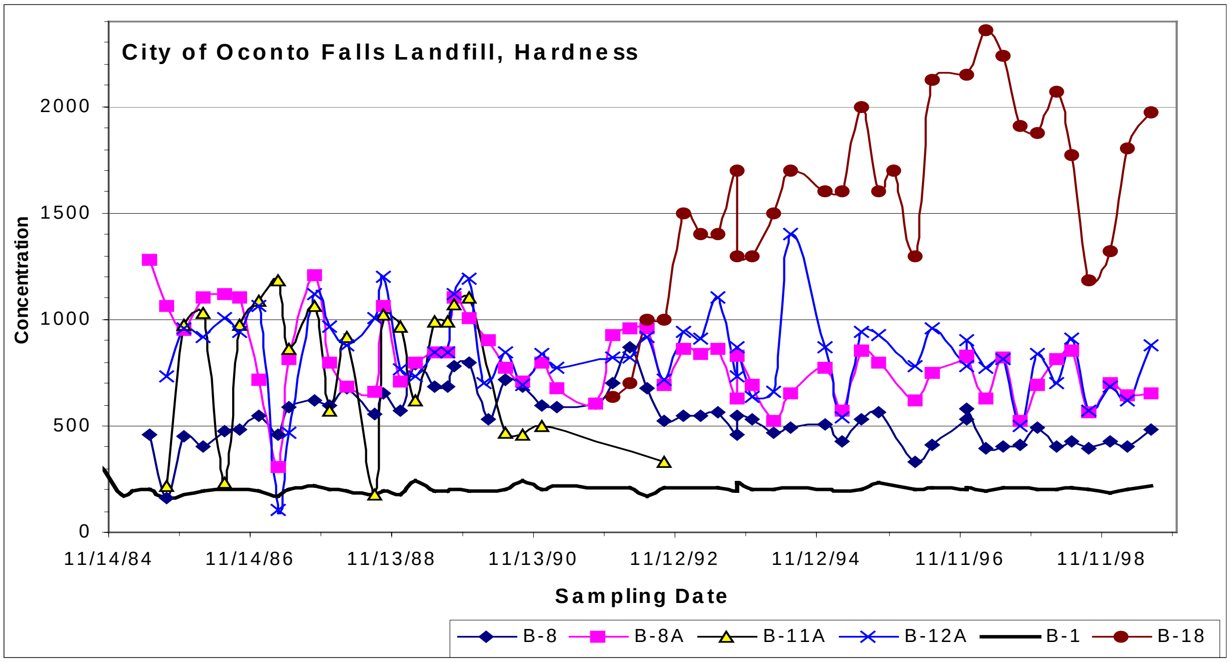



FIGURE A1 - 2F: TIME VS. CONCENTRATION GRAPH OF HARDNESS DATA FOR THE OCONTO FALLS LANDFILL.



## Weyerhaeuser Company Landfill

A site that falls into the *COD Not Effective / Other Parameters Effective* category is the Weyerhaeuser Company Landfill, a paper mill sludge landfill. Groundwater monitoring data for Weyerhaeuser Company Landfill are displayed in time versus concentration graphs in Figures 3a-g. Overall impacts are pretty clear in most of the data, but no consistent trend is seen among the parameters. The upgradient well used for comparing the data is W-1.

Ammonia nitrogen data over time is shown in Figure 3A. The data are somewhat disconnected and levels are not too high. Figure 3B is the time versus concentration graph for alkalinity data. An overall impact in downgradient wells is fairly clear, especially when comparing upgradient well W-1 to downgradient W-2B. COD data are shown in Figure 3C, and the data show a slight increasing trend but not an overall impact. Sample results from the upgradient well are too similar to the results for the downgradient wells. Without a clear overall impact, COD is not identifying the contamination. Figure 3D displays conductivity data for the Weyerhaeuser Company Landfill. Similar to alkalinity data, the conductivity data shows overall impacts between upgradient well, W-1, and downgradient wells, especially W-2A and W-2B. Hardness data is seen in Figure 3E. Outliers were removed to better display the data. Overall impacts are seen by the clear separation of data between upgradient well, W-1, and downgradient well, W-2B. Figure 3F shows the data for nitrate + nitrite as N. No trends or overall impacts are apparent, but much of the data exceeds the public health standard of 2 for nitrate + nitrite as N. An outlier value of 110 was removed from the nitrate + nitrite as N data. Finally, sulfate data is seen in Figure 3G. A decreasing trend is shown, which does not match any of the other parameters. Additionally, an overall impact between the upgradient well, W-1, and the downgradient wells is not really seen since the values are very similar. The fact that the PAL value of 125 is exceeded by all wells is the only indication of a problem from sulfate data. See Appendix 2 for a summary of results for this site.

The Weyerhauser Company Landfill is a good example of how COD was not identifying the contamination, and other parameters were somewhat confusing. However, when the other parameters were looked at in detail, the overall impacts between the upgradient well and the downgradient wells were clear.

FIGURE A1 - 3A: TIME VS. CONCENTRATION GRAPH OF AMMONIA NITROGEN DATA FOR THE WEYERHAEUSER COMPANY LANDFILL

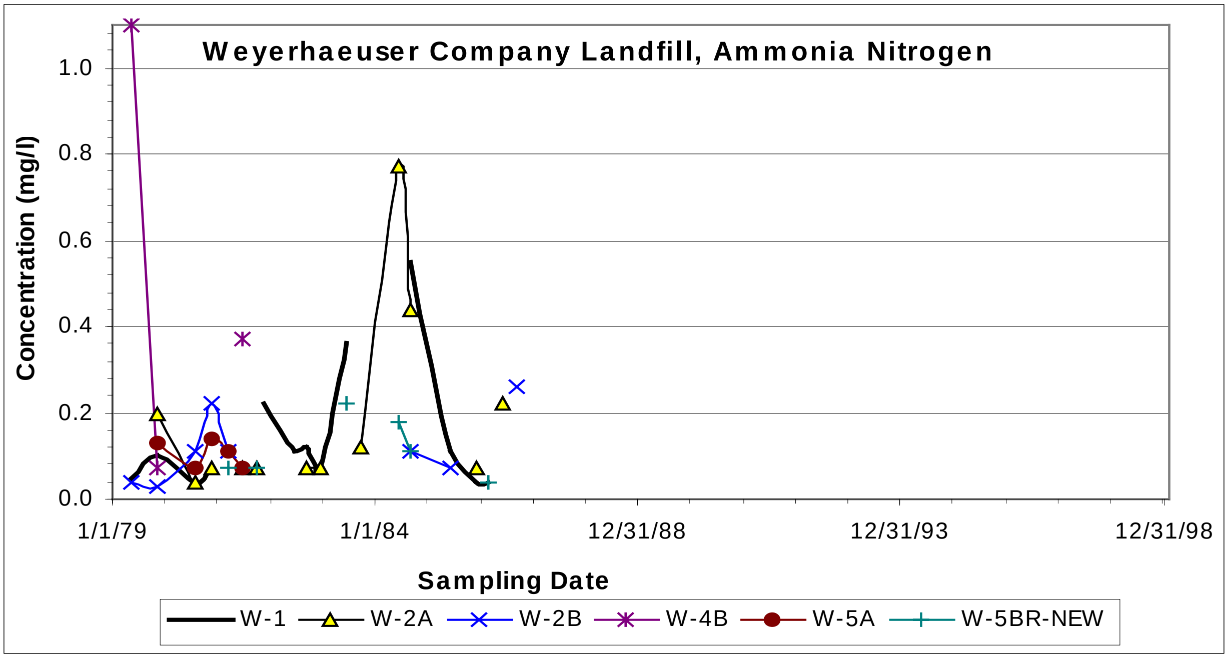



FIGURE A1 - 3B: TIME VS. CONCENTRATION GRAPH OF ALKALINITY DATA FOR THE WEYERHAEUSER COMPANY LANDFILL.

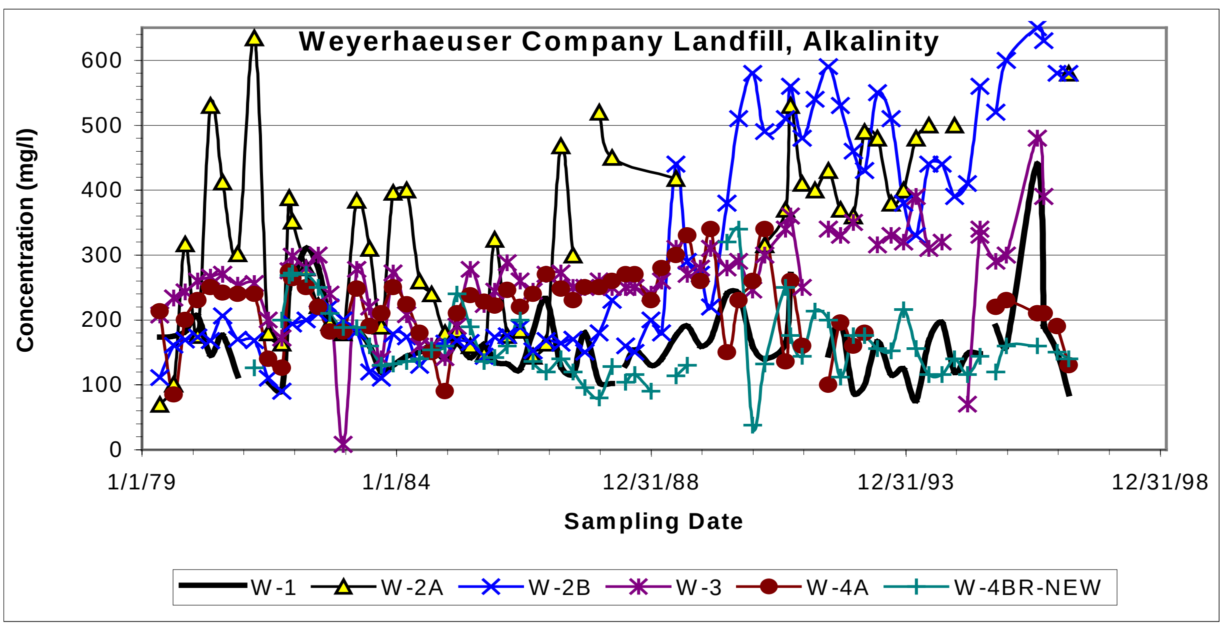


FIGURE A1 - 3C: TIME VS. CONCENTRATION GRAPH OF COD DATA FOR THE WEYERHAEUSER COMPANY LANDFILL.

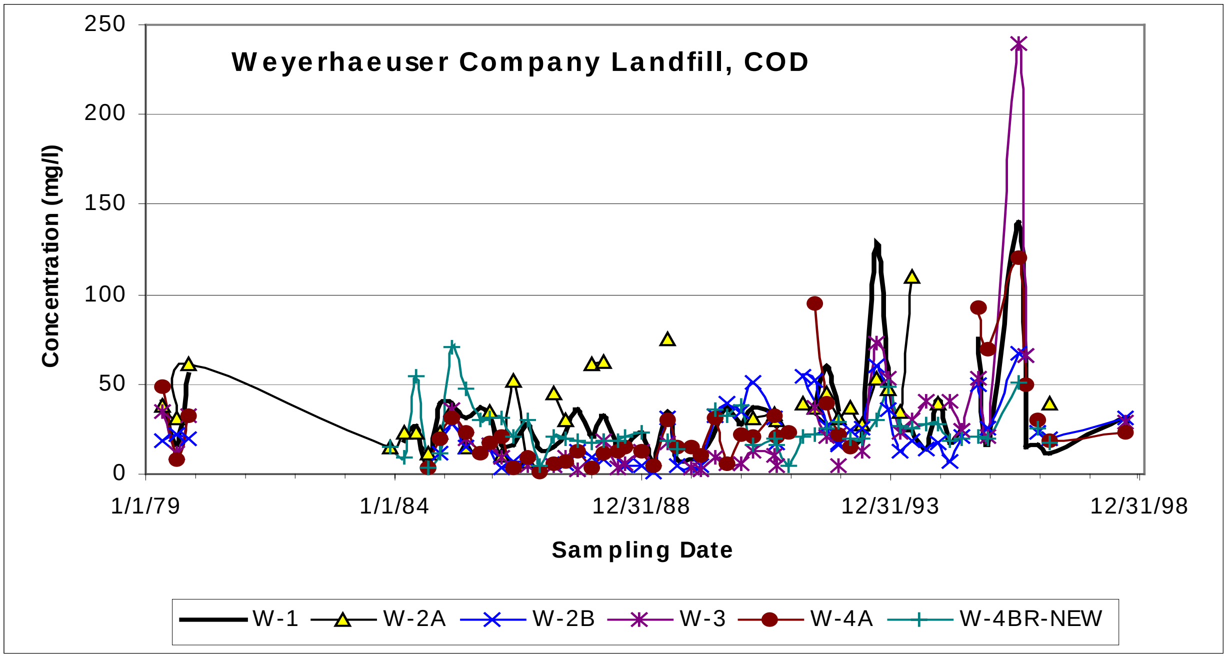



FIGURE A1 - 3D: TIME VS. CONCENTRATION GRAPH OF CONDUCTIVITY DATA FOR THE WEYERHAEUSER COMPANY LANDFILL.

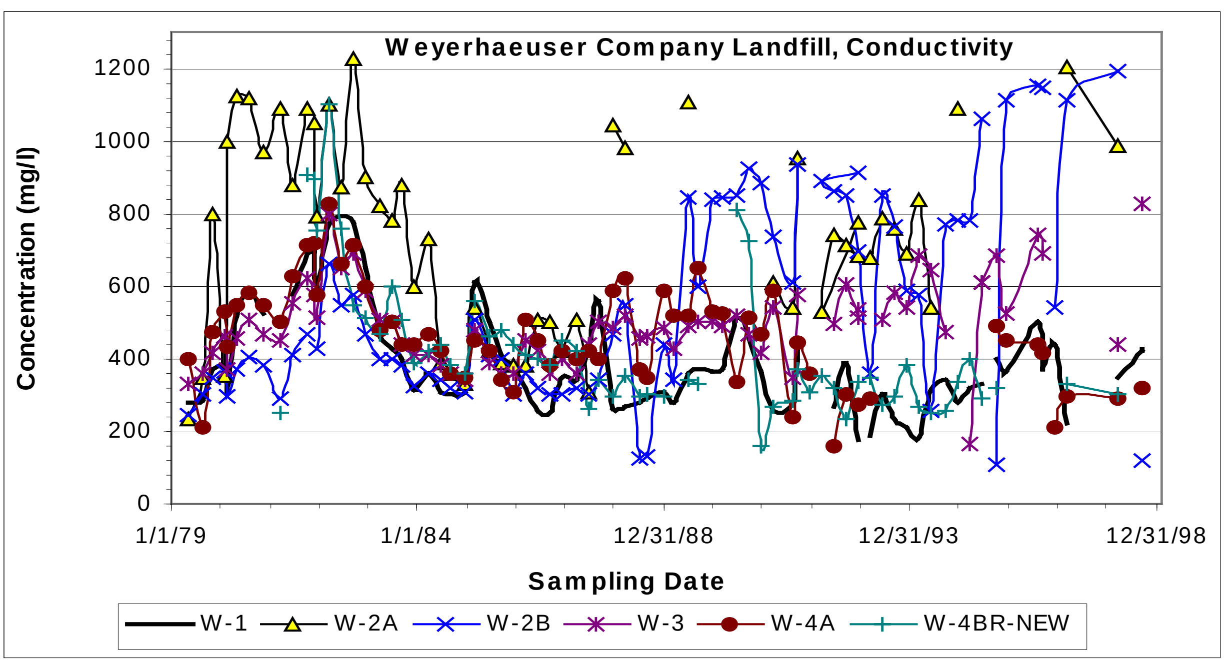


FIGURE A1 - 3E: TIME VS. CONCENTRATION GRAPH OF HARDNESS DATA FOR THE WEYERHAEUSER COMPANY LANDFILL.

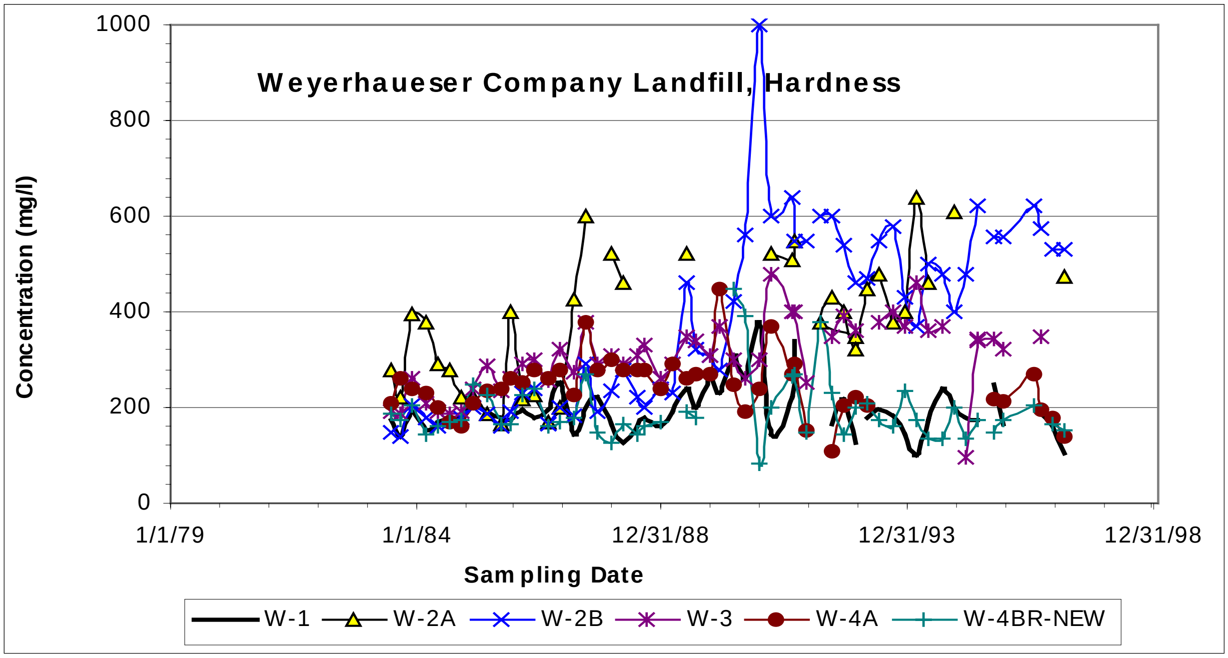



FIGURE A1 - 3F: TIME VS. CONCENTRATION GRAPH OF NITRATE+NITRITE DATA FOR THE WEYERHAEUSER COMPANY LANDFILL.

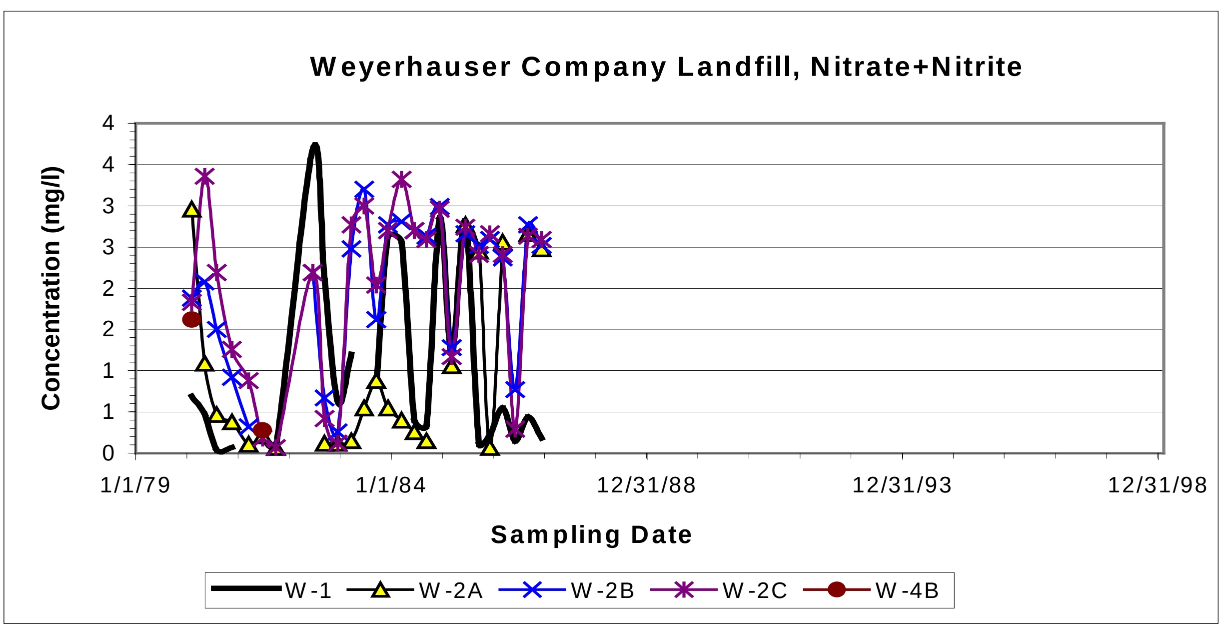
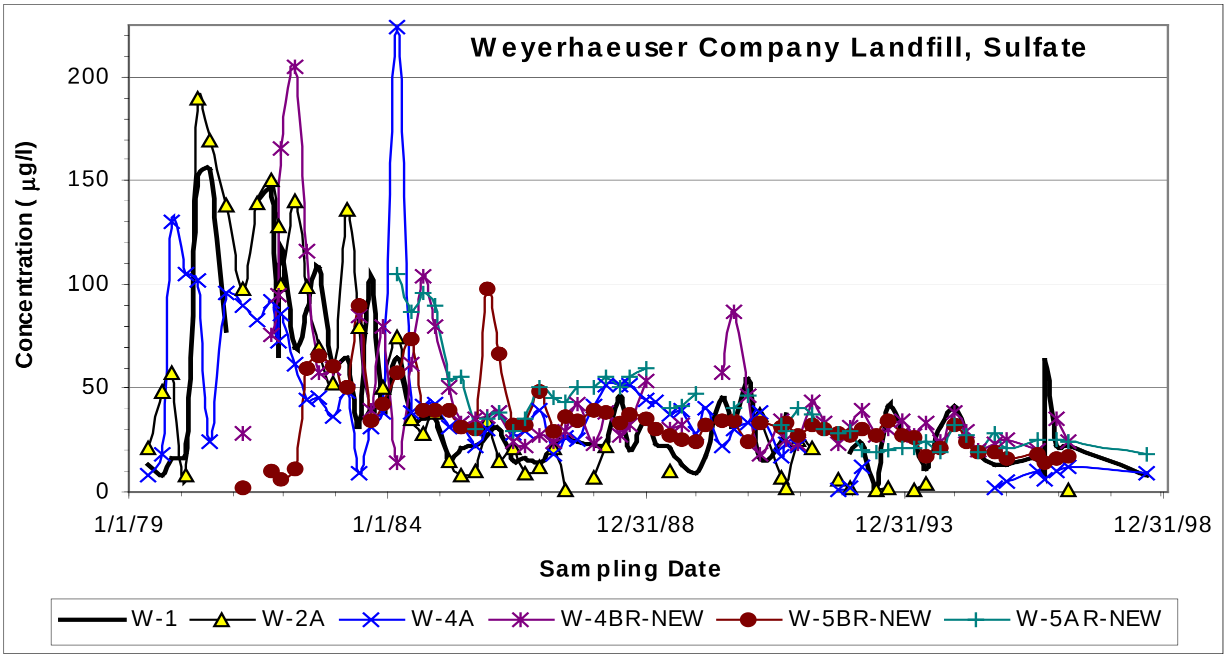


FIGURE A1 - 3G: TIME VS. CONCENTRATION GRAPH OF SULFATE DATA FOR THE WEYERHAEUSER COMPANY LANDFILL



## City of Wauwatosa Landfill

The City of Wauwatosa Landfill accepted mostly incinerator ash from municipal waste during its operation. However, other waste was also accepted at this landfill so it is not truly a Municipal Solid Waste Combustor Residue landfill. Groundwater monitoring occurred after contamination had been discovered at this old, closed site.

Figures 4A-H show groundwater monitoring data over time for the City of Wauwatosa Landfill. The summary sheet in Appendix 2 shows decisions made on the usefulness of all monitoring parameters.

In Figure 4A, a clear overall impact between upgradient well MW-7 and the other wells. MW-7 shows a steady concentration, which makes it a good reference well to compare the downgradient wells to. The other wells have significantly higher concentration levels for alkalinity. None of the other wells show an increase in alkalinity concentration, but this is expected because monitoring occurred long after the landfill began accepting waste. The overall impact decision is indicated on the summary sheet.

Figure 4B is not very helpful due to the lack of data for cadmium at this site. This graph was included mainly because the sample results for MW-2 exceed the public health standard of 0.5. However, the lack of data makes this parameter questionable, and it is not convincing evidence of contamination at this site.

Chloride data are shown in Figure 4C. The calculated PAL (125) is indicated on the graph, and MW-7 shows the background levels. MW-2 and MW-6 appear to have increasing concentrations of chloride over time. MW-1 has a slight decrease, and MW-3R has levels below the background levels established from MW-7. Both increases and overall impacts are indicated for chloride data on the summary sheet. Contamination is clearly present from the chloride data despite the low levels from MW-3R, especially when the concentrations in the other wells far exceed the enforcement standard (ES) of 250.

Figure 4D shows COD data for the City of Wauwatosa Landfill. This data was neither useful nor not useful. Mainly the data was confusing overall but a slight overall impact could be seen. The problem with the COD data is the large variations in the levels for upgradient well MW-7. MW-7 has almost as high levels as all the other wells. A slight overall impact is seen more in the most recent data. Overall, COD was somewhat useful but not convincing.

The time versus concentration graph for conductivity data is Figure 4E. Overall, the data are showing high levels and higher levels than those seen in background well MW-7.

However, the lack of data for MW-7 raise questions on comparing the impacts seen in the downgradient wells. An overall impact was seen for conductivity data because of the high concentration values for all wells.

Hardness data (Figure 4F) show similar trends and impacts to alkalinity data for this site. Upgradient well, MW-7, shows fairly steady levels. Despite the lower levels seen from MW-3R (similar to chloride and alkalinity data), all other wells are showing clearly higher concentrations. Thus, hardness data show an overall impact and identified the contamination.

Figure 4G, showing lead data, is significant because many wells had readings exceeding the public health standard of 1.5. The overall impact seen from lead was noted on the summary sheet and the data appeared to be a flag for detecting contamination at this site.

Figure 4H shows sulfate data for the City of Wauwatosa Landfill. No decision was made as to whether an impact or trends were seen from the sulfate data because of the high background levels seen in MW-7. With only one well (MW-2) higher than MW-7, the data was not useful in determining whether contamination was present.

The City of Wauwatosa Landfill was a good example of how the COD could be useful or not useful depending on the interpretation of the data. Therefore, a label of somewhat useful was given to the COD data. Even though COD data were not convincing at identifying the contamination, many other parameters (alkalinity, cadmium, conductivity, hardness, and lead) identified the contamination clearly. Additionally, many VOC exceedances were discovered even at the beginning of groundwater monitoring.

FIGURE A1 - 4A: TIME VS. CONCENTRATION GRAPH OF ALKALINITY DATA FOR THE CITY OF WAUWATOSA LANDFILL.

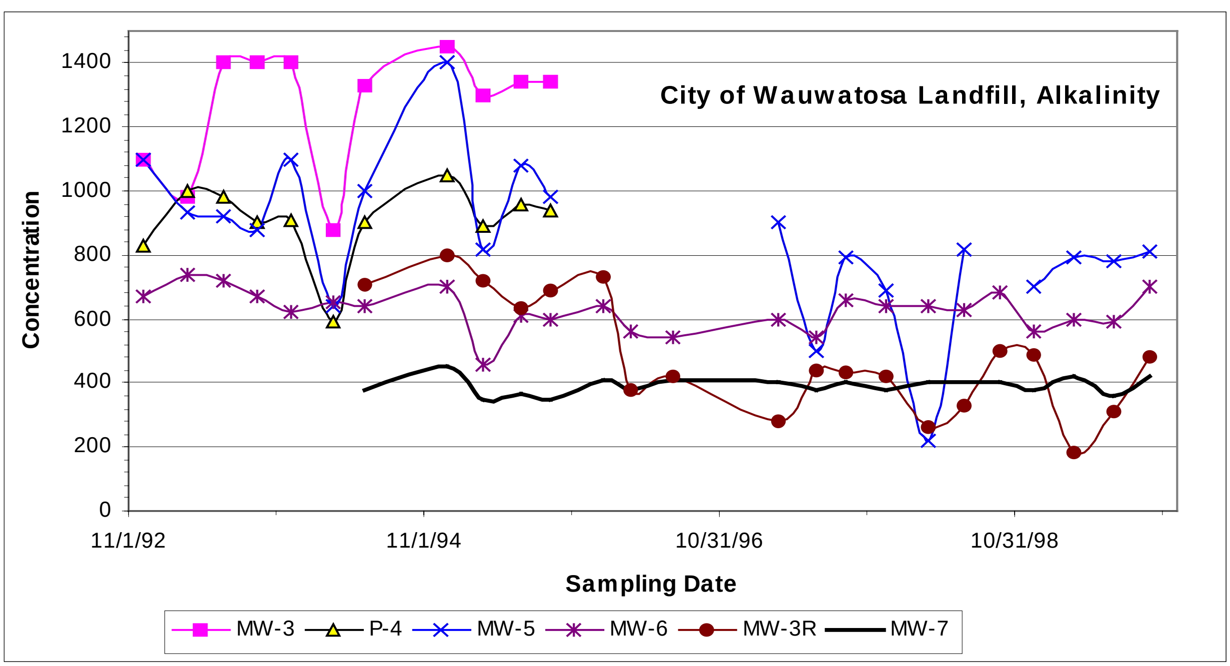


FIGURE A1 - 4B: TIME VS. CONCENTRATION GRAPH OF CADMIUM DATA FOR THE CITY OF WAUWATOSA LANDFILL.

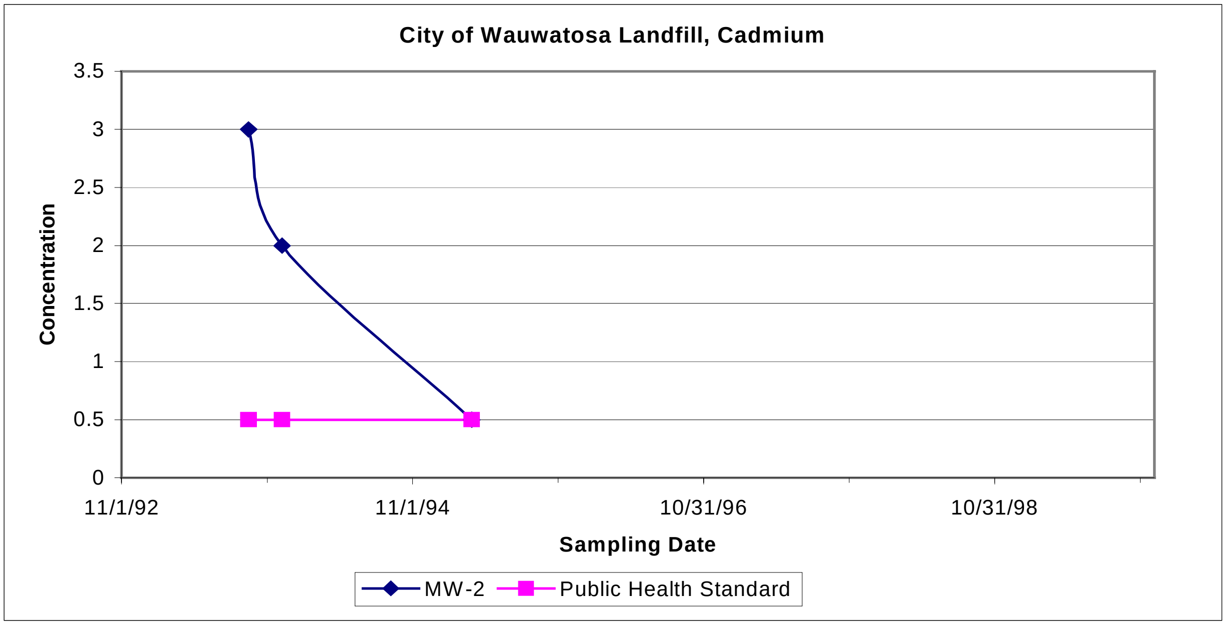



FIGURE A1 - 4C: TIME VS. CONCENTRATION GRAPH OF CHLORIDE DATA FOR THE CITY OF WAUWATOSA LANDFILL.

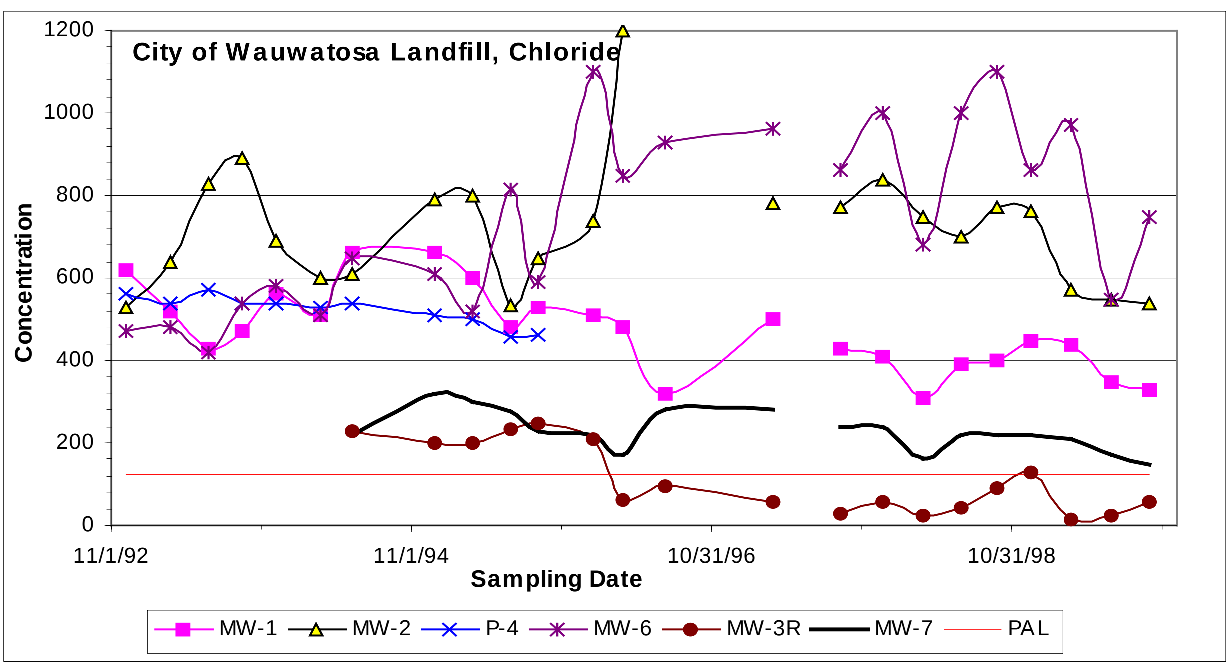


FIGURE A1 - 4D: TIME VS. CONCENTRATION GRAPH OF COD DATA FOR THE CITY OF WAUWATOSA LANDFILL.

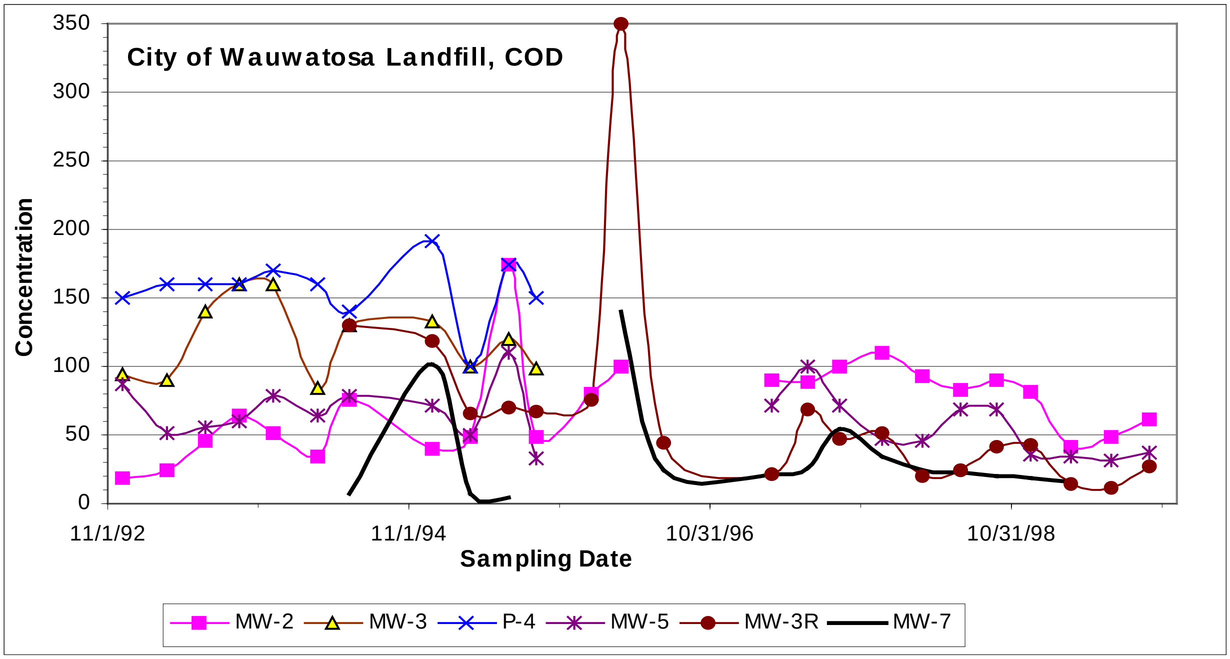



FIGURE A1 - 4E: TIME VS. CONCENTRATION GRAPH OF CONDUCTIVITY DATA FOR THE CITY OF WAUWATOSA LANDFILL.

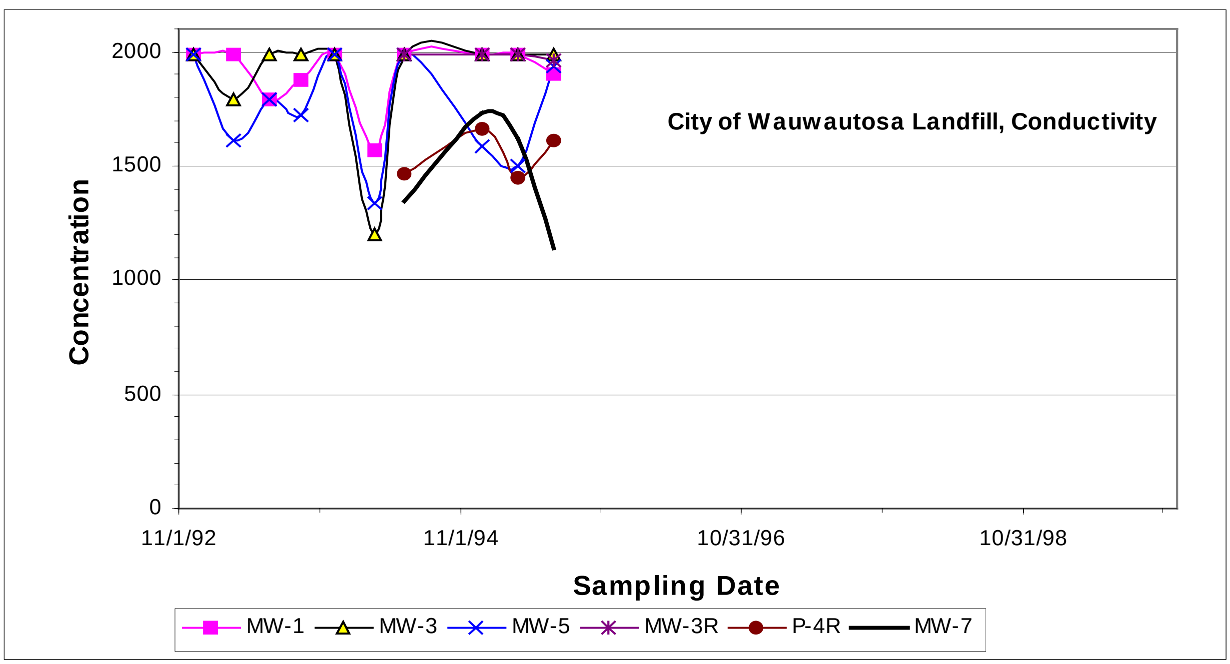


FIGURE A1 - 4F: TIME VS. CONCENTRATION GRAPH OF HARDNESS DATA FOR THE CITY OF WAUWATOSA LANDFILL.

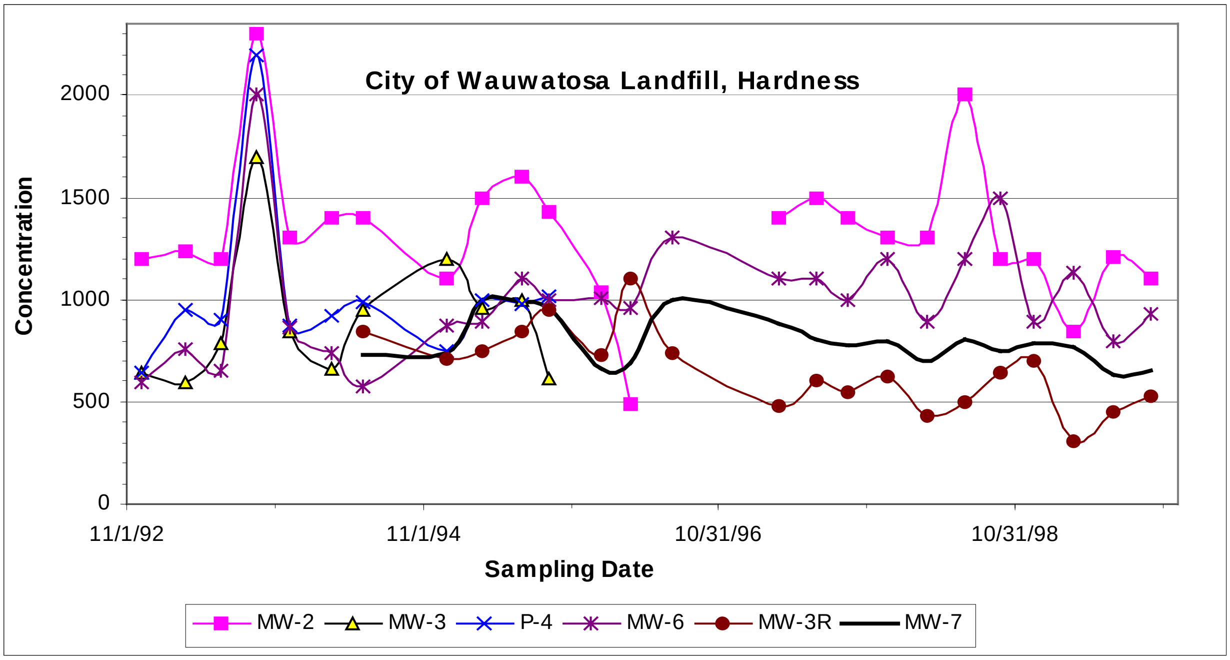



FIGURE A1 - 4G: TIME VS. CONCENTRATION GRAPH OF LEAD DATA FOR THE CITY OF WAUWATOSA LANDFILL.

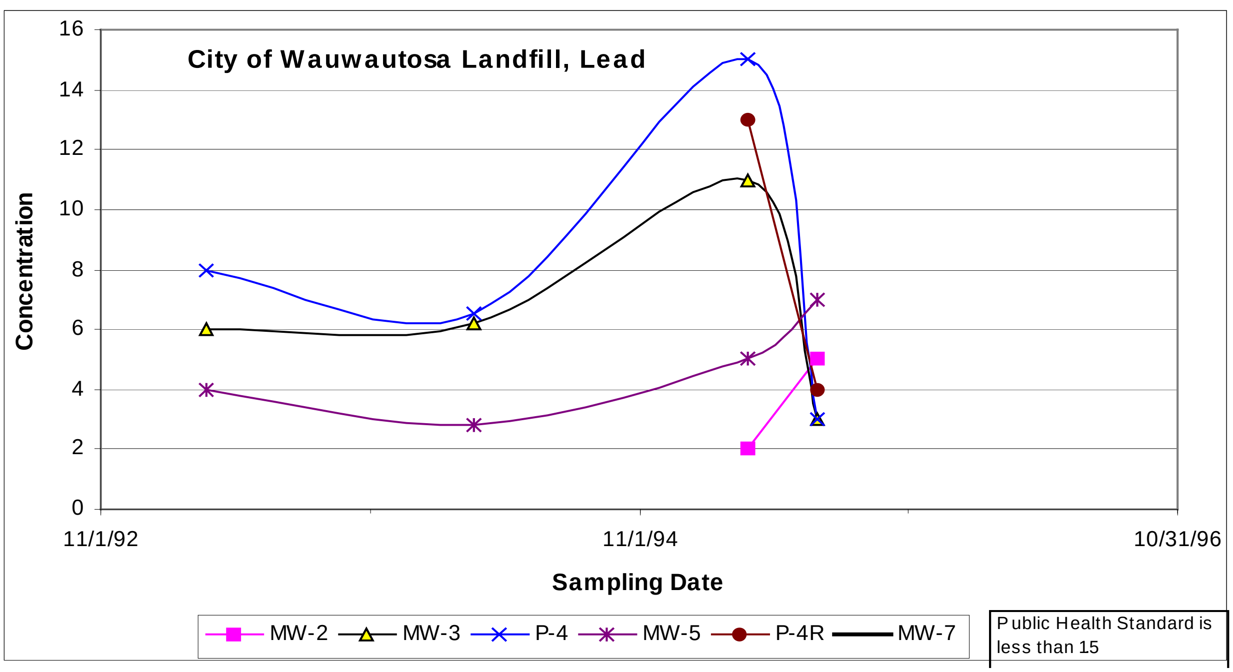
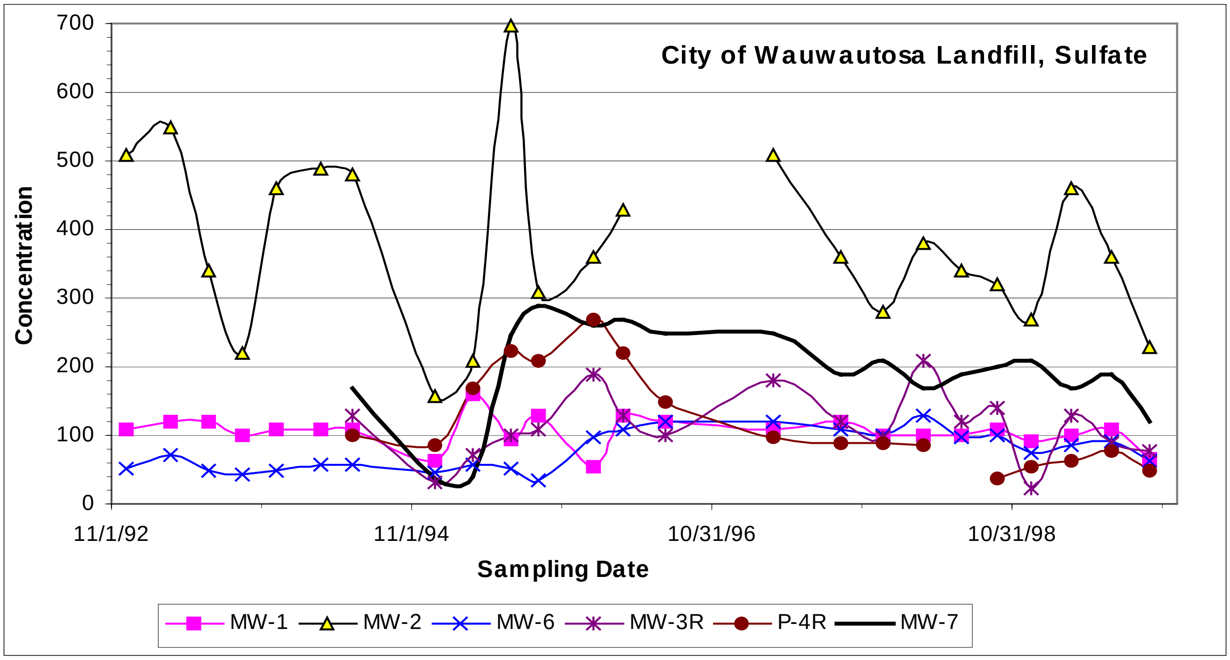


FIGURE A1 - 4H: TIME VS. CONCENTRATION GRAPH OF SULFATE DATA FOR THE CITY OF WAUWATOSA LANDFILL.



## WEPCO Cedar Sauk Landfill

Groundwater monitoring requirements for the WEPCO Cedar Sauk Landfill did not include COD. Because the WEPCO Cedar Sauk Landfill is a fly or bottom ash landfill, organic material is not expected to be present. VOC sampling also did not occur at this site.

Figures 5A - D are the time versus concentration graphs for boron, conductivity, hardness, and sulfate. W-1A is the upgradient well used to establish background groundwater quality, and data for this well are represented by a thick solid line. For all parameters, clear overall impacts were noted between W-1A and the downgradient wells. Also, slight increases in concentrations were observed for conductivity, hardness, and sulfate, especially in wells P-2A and W-4.

The WEPCO Cedar Sauk Landfill is an excellent example of a site that did not need COD to detect contamination. This most likely is because the type of landfill decreases the need for monitoring organic material.

FIGURE A1 - 5A: TIME VS. CONCENTRATION GRAPH OF BORON DATA FOR THE WEPCO CEDAR SAUK LANDFILL.

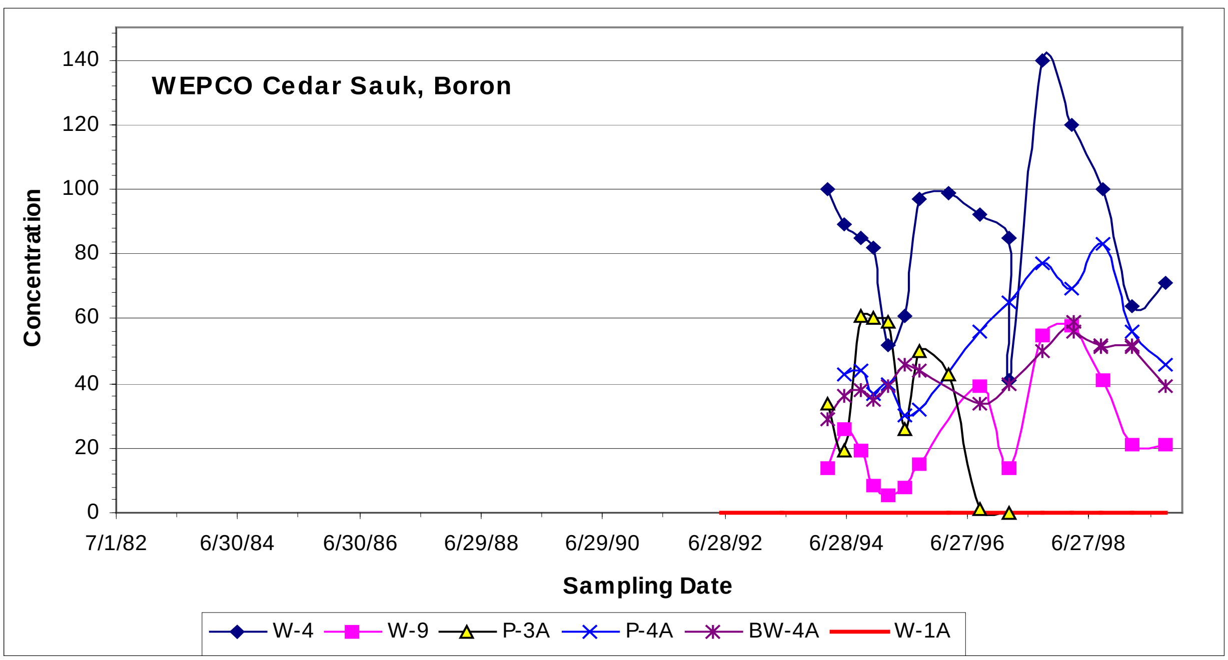


FIGURE A1 - 5B: TIME VS. CONCENTRATION GRAPH OF CONDUCTIVITY DATA FOR THE WEPCO CEDAR SAUK LANDFILL.

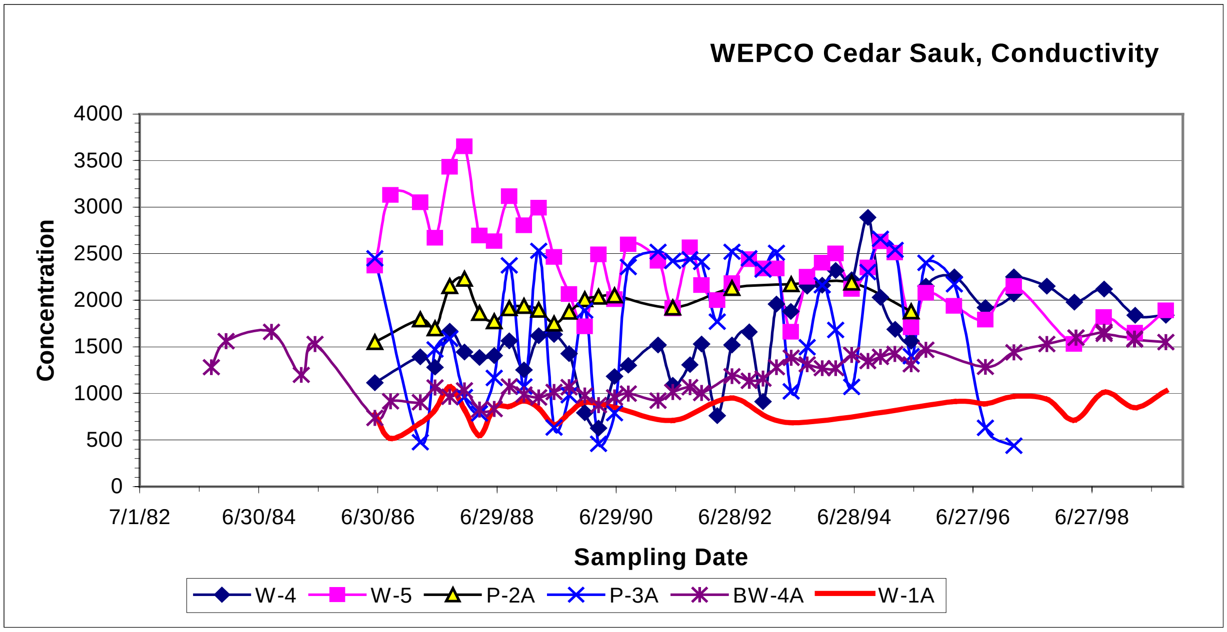



FIGURE A1 - 5C: TIME VS. CONCENTRATION GRAPH OF HARDNESS DATA FOR THE WEPCO CEDAR SAUK LANDFILL.

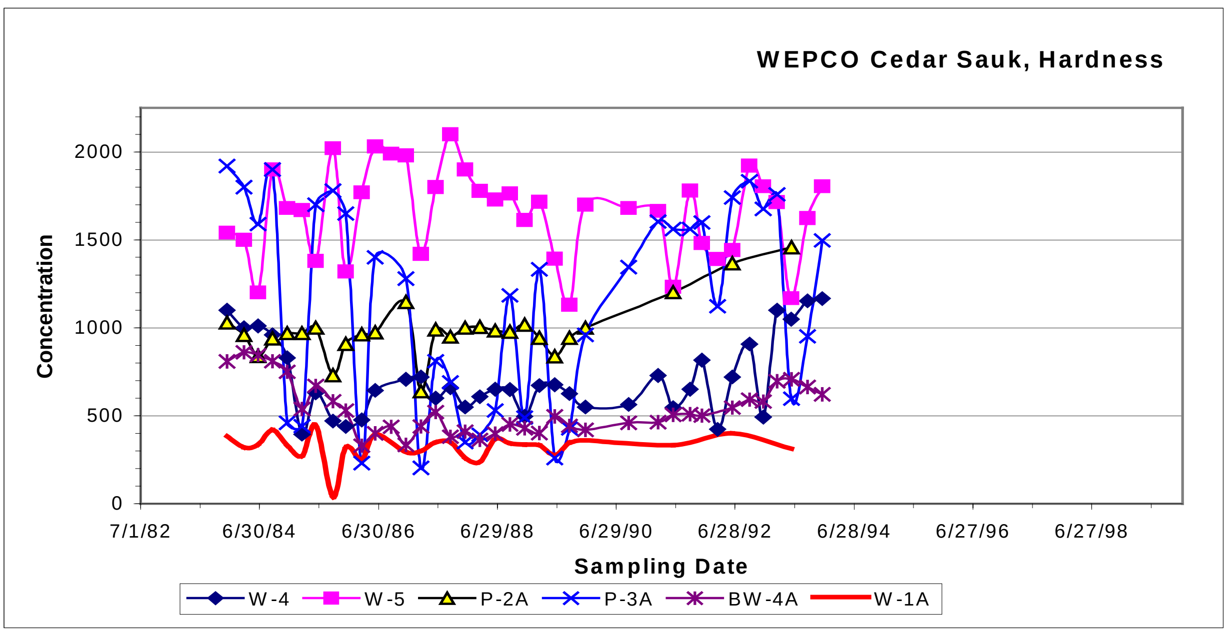
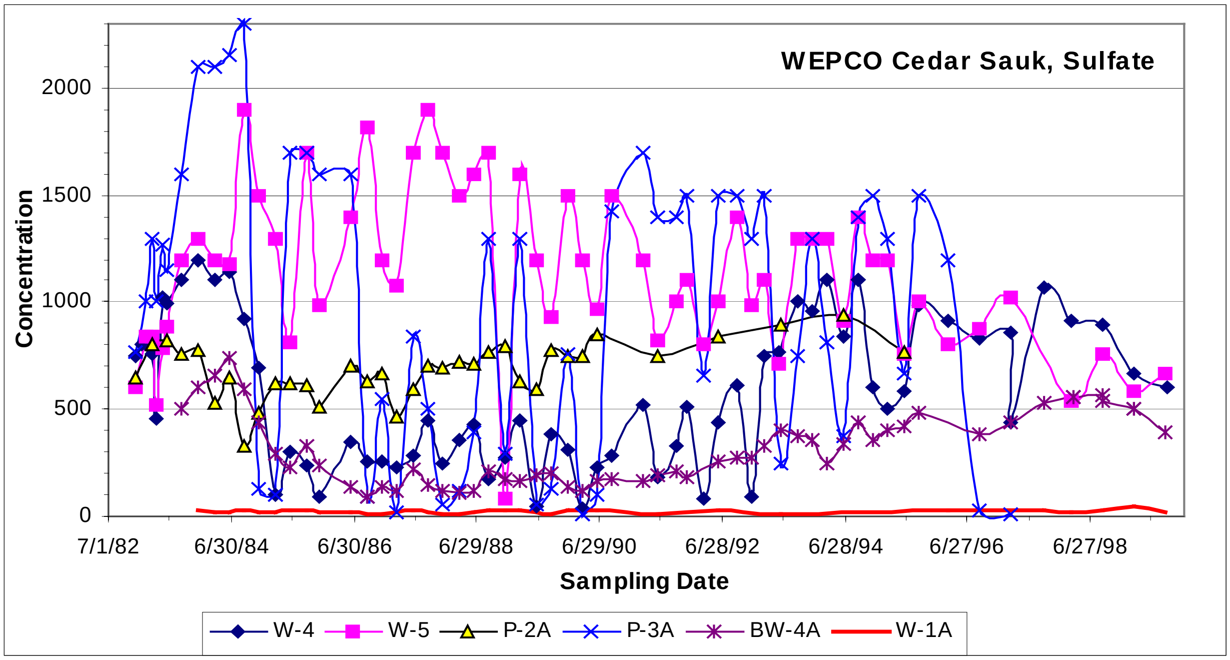


FIGURE A1 - 5D: TIME VS. CONCENTRATION GRAPH OF SULFATE DATA FOR THE WEPCO CEDAR SAUK LANDFILL.



## Refuse Hideaway Landfill

Groundwater monitoring data for the Refuse Hideaway landfill is lacking. Figures 6A-D show sampling results over time for the following parameters: alkalinity, chloride, conductivity, pH, and hardness. This site had no data for COD. Upgradient wells for this site were P-23S and P-20SR. An argument could be made that there is an overall impact seen by comparing the other wells to P-23S, but due to the lack of data, the parameters were not useful. However, when a VOC summary was run, most of the wells for the entire site, not just the small sample selected for the time versus concentration graphs, showed many exceedances.

The reason why the indicator parameters did not show the contamination is because the Refuse Hideaway landfill is underlain by fractured dolomite. The contamination "disappeared" into the fractures. DNAPLS remained and were identified by VOC testing. Once the contamination was discovered, the site discontinued monitoring for the indicator parameters.

FIGURE A1 - 6A: TIME VERSUS CONCENTRATION GRAPH FOR ALKALINITY DATA AT THE REFUSE HIDEAWAY LANDFILL.

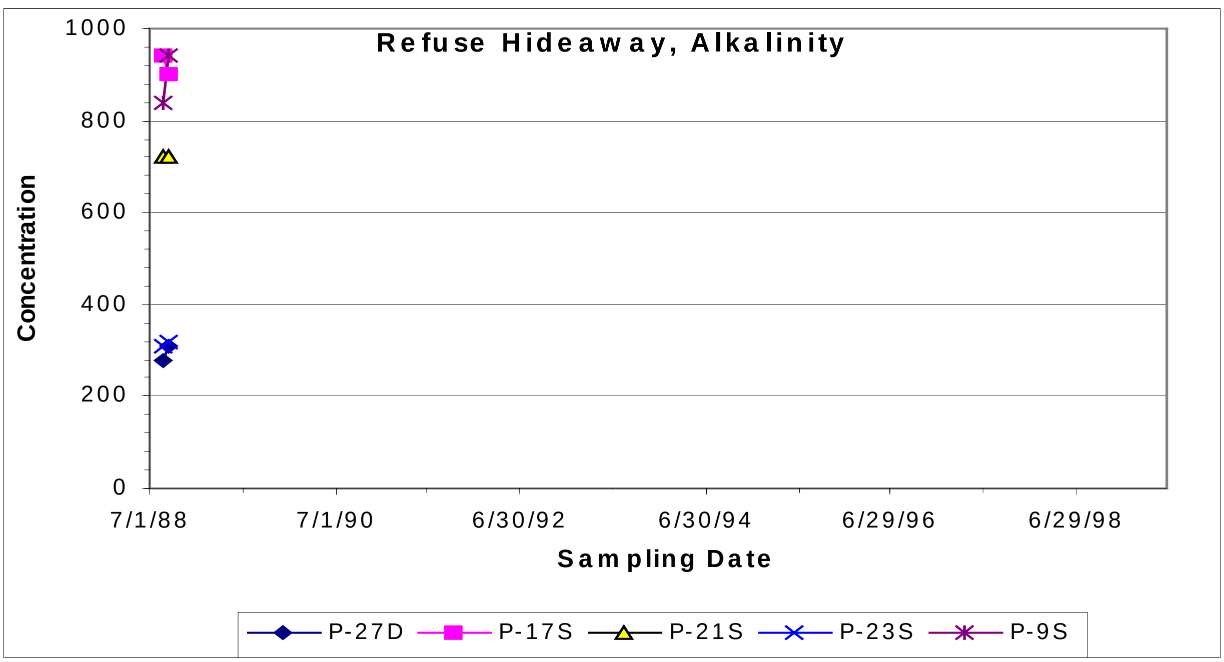


FIGURE A1 -6B: TIME VERSUS CONCENTRATION GRAPH FOR CHLORIDE DATA AT THE REFUSE HIDEAWAY LANDFILL.

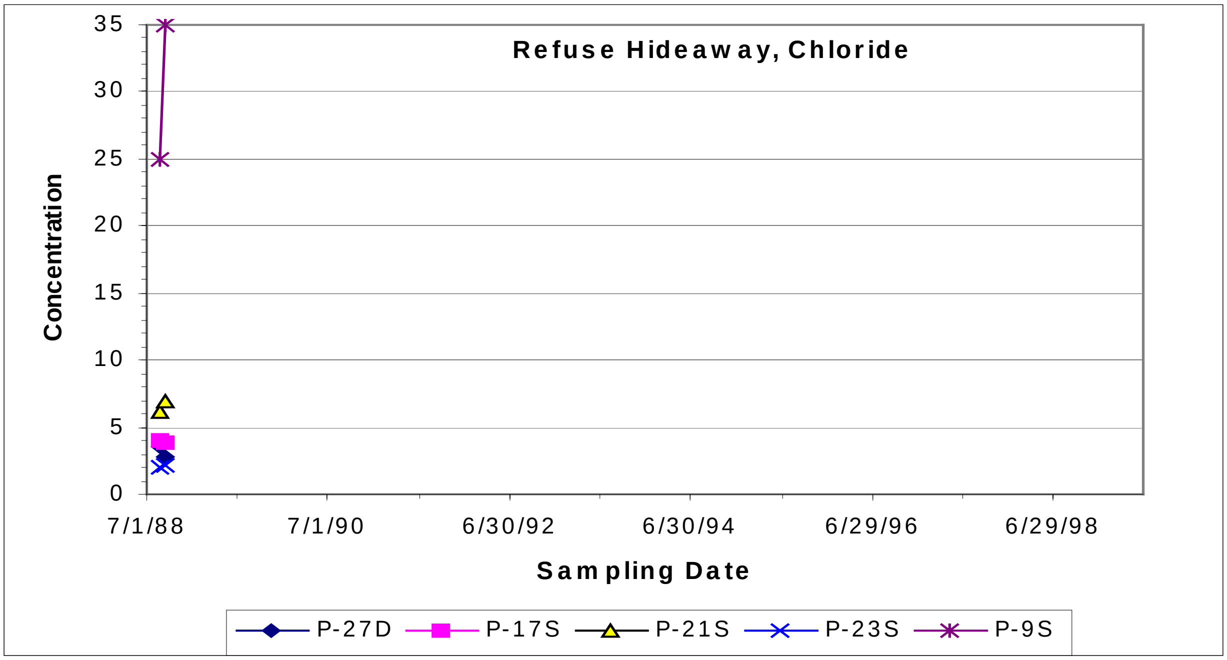



FIGURE A1 - 6C: TIME VERSUS CONCENTRATION GRAPH FOR CONDUCTIVITY DATA AT THE REFUSE HIDEAWAY LANDFILL.

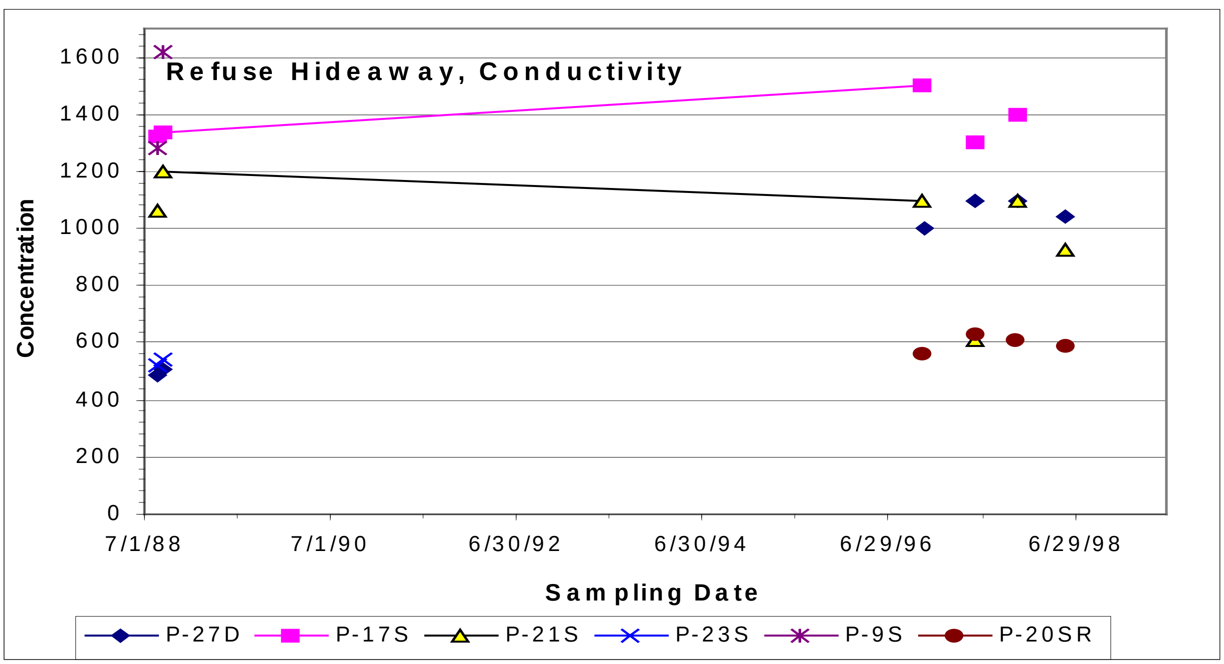
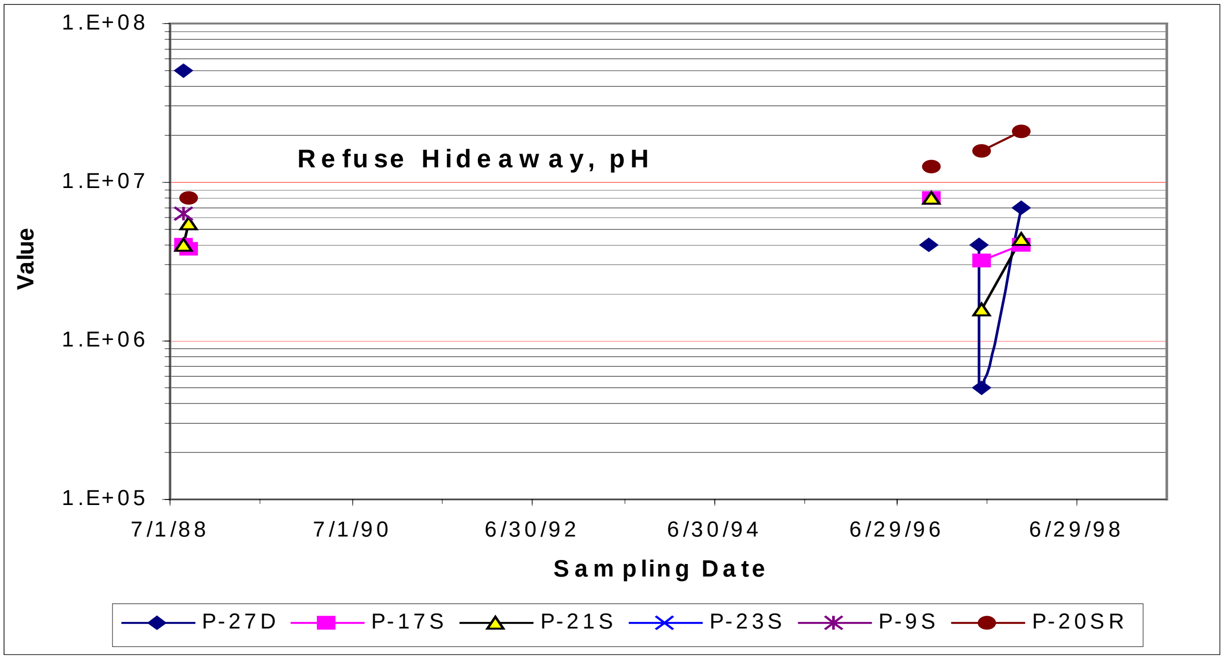


FIGURE A1 - 6D: TIME VERSUS CONCENTRATION GRAPH FOR PH DATA AT THE REFUSE HIDEAWAY LANDFILL.



## Wausau Papers Landfill

Wausau Papers Landfill was suggested as a contaminated site with an unlined portion that had plenty of data that may be useful. Cell 1 of the Wausau Papers Landfill was licensed in 1973 under the license number 2038, and the cell was unlined. A clay lined cell (Cell 2, license number 2875) began operating in 1981 and also contained a leachate collection system. In 1983, Cell 1 stopped accepting waste, and in mid 1983, an equipment breakdown caused a increase in sludge volume and prematurely "filled" Cell 2. Cell 1 closure was completed in 1985, which included installation of a landfill gas collection system. Also in 1985, a vertical expansion of Cell 2 was approved. A second expansion of Cell 2 was approved in 1986. A third cell began operating in 1987 (license number 3115). In 1988, Cell 2 operation ends and remediation efforts were reported. In June of 1989, vandalism of wells P-1, P-3, P-4, and P-5 was documented. These wells were contaminated with petroleum based products, which caused problems with the groundwater monitoring data.

Data used for time versus concentration graphs are under license number 2875, which is representative of both Cell 1 and Cell 2 groundwater monitoring data due to the direction of groundwater flow. Well P-13 is the upgradient well used to represent background groundwater quality for the site. Figures 7A - F show the time versus concentration graphs for groundwater monitoring indicator parameters.

COD (Figure 7C) does not appear to be a useful parameter at this site other than showing overall impacts. Data jump around, with some peaks correlating to significant events such as the closure of Cell 1, increased volume of sludge due to equipment failure, and vandalism in a few wells. Alkalinity (Figure 7A) and hardness (Figure 7E) data show similar trends as COD, even with similar peaks. Chloride (Figure 7B) and sulfate (Figure 7F) did show generally increasing trends. Conductivity (Figure 7D) data is misleading because the high levels are seen only in leachate collection wells (MH#1 and MH#5). The data for this site is complicated due to the many expansions of the landfill. The parameters show overall impacts between upgradient and downgradient wells, but only a few of the parameters show increasing contamination with time.

VOCs were prevalent at this site, but the wells showing the most VOC contamination did not match those wells showing contamination from the indicator parameters. Since the data is confusing for indicator parameters and VOCs, COD may be useful for this site in showing overall impacts. However, it is obvious that this is a contaminated site, and COD is not the only parameter identifying the contamination.

FIGURE A1 - 7A: TIME VERSUS CONCENTRATION GRAPH OF ALKALINITY DATA FOR THE WAUSAU PAPER MILLS LANDFILL.

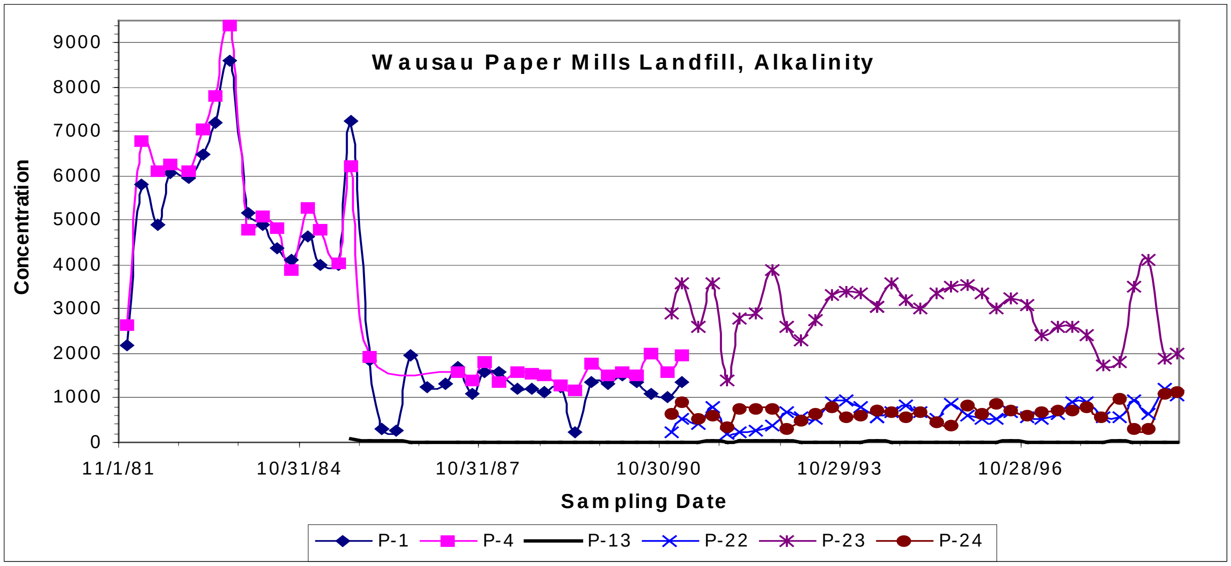



FIGURE A1 - 7B: TIME VERSUS CONCENTRATION GRAPH OF CHLORIDE DATA FOR THE WAUSAU PAPER MILLS LANDFILL.

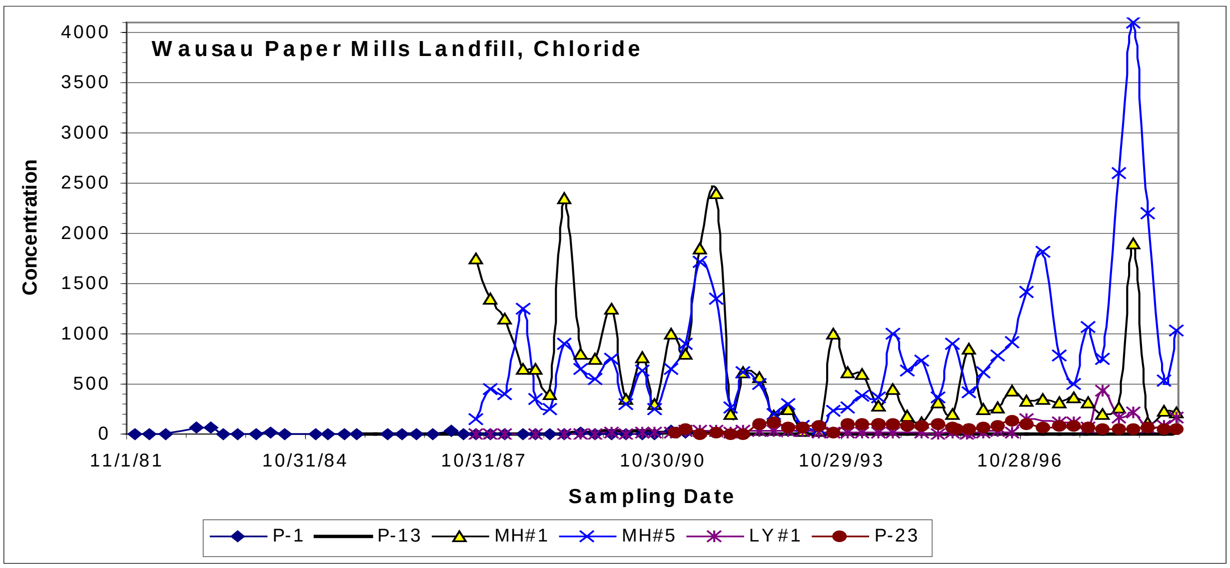


FIGURE A1 - 7C: TIME VERSUS CONCENTRATION GRAPH OF COD DATA FOR THE WAUSAU PAPER MILLS LANDFILL.

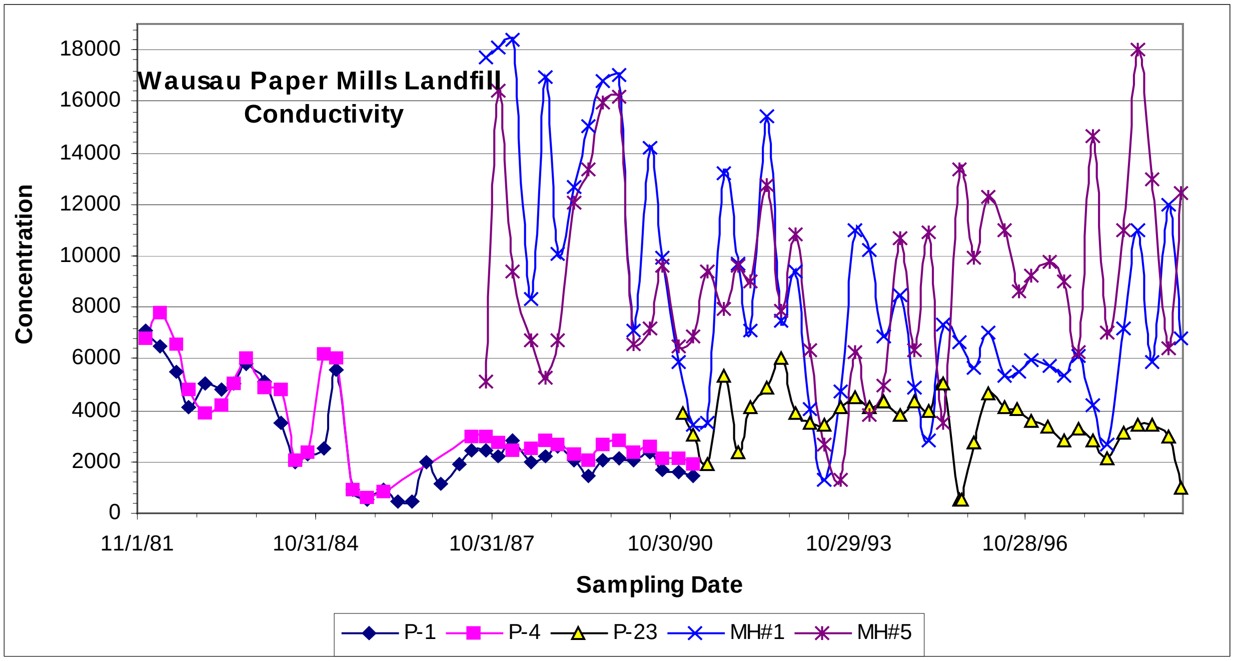



FIGURE A1 - 7D: TIME VERSUS CONCENTRATION GRAPH OF CONDUCTIVITY DATA FOR THE WAUSAU PAPER MILLS LANDFILL.

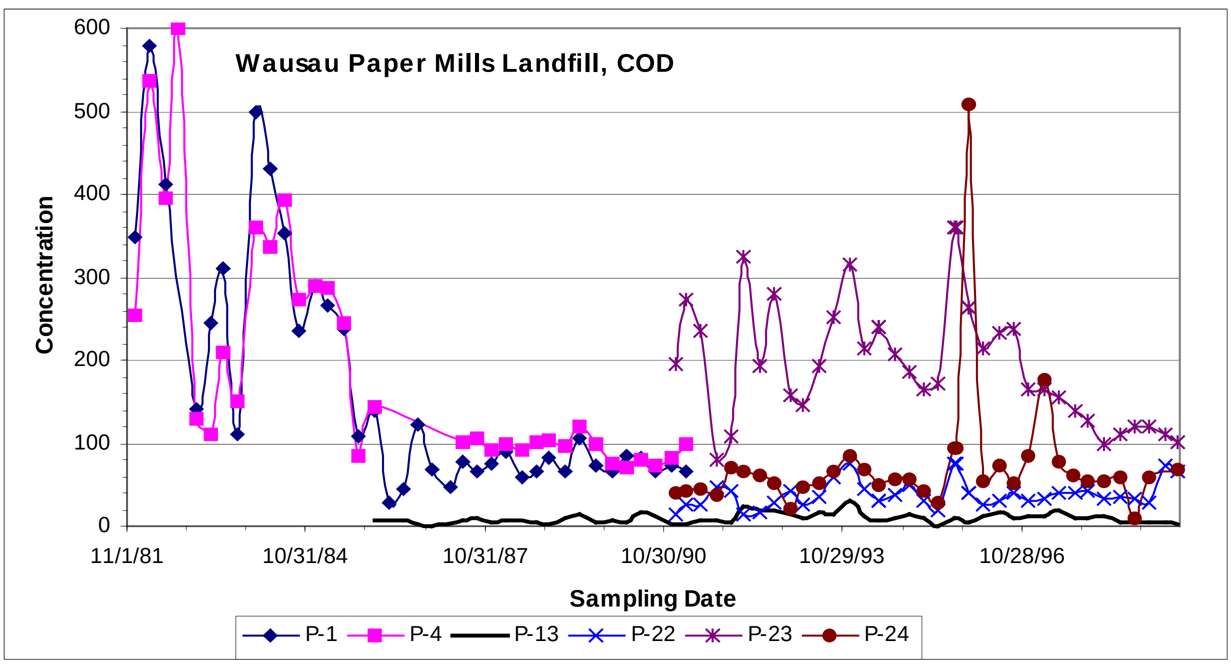


FIGURE A1 - 7E: TIME VERSUS CONCENTRATION GRAPH OF HARDNESS DATA FOR THE WAUSAU PAPER MILLS LANDFILL.

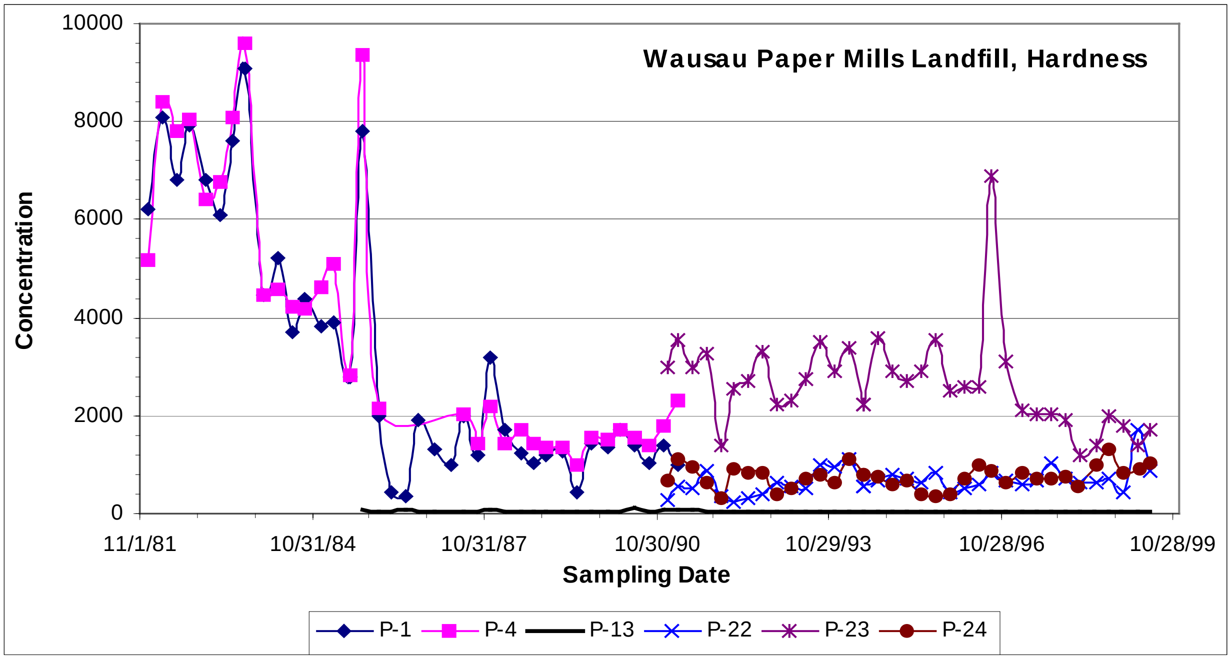
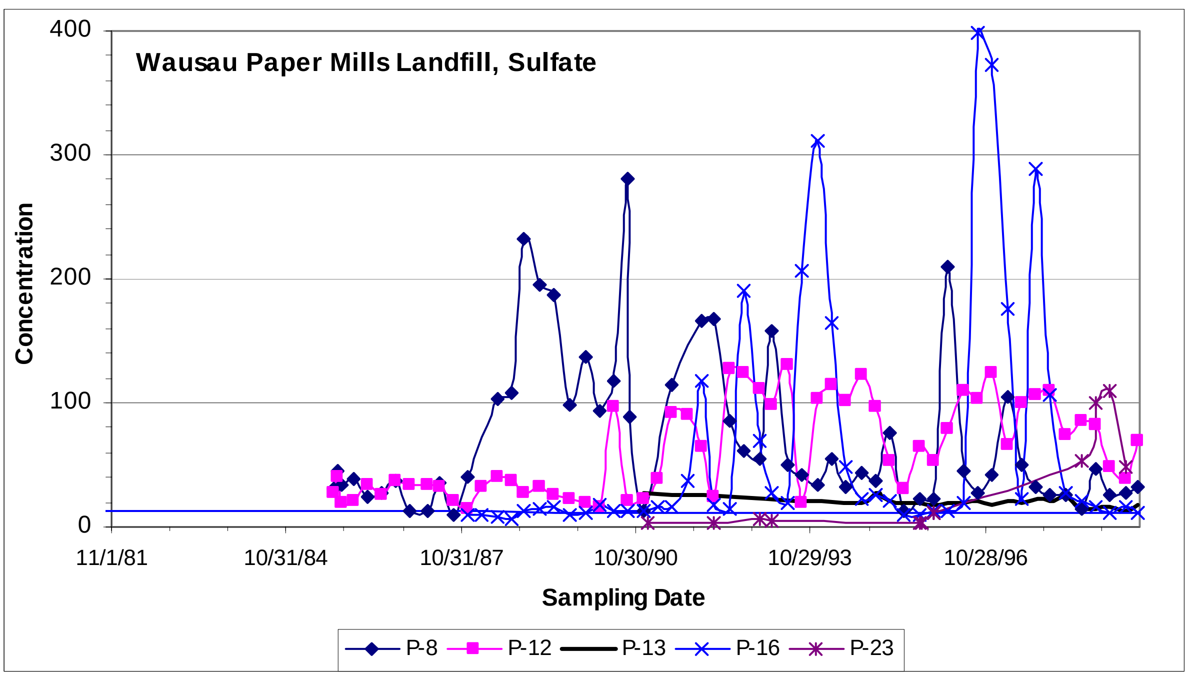



FIGURE A1 - 7F: TIME VERSUS CONCENTRATION GRAPH OF SULFATE DATA FOR THE WAUSAU PAPER MILLS LANDFILL.



## Appendix 2: Summary Sheets

## Site Name: Flambeau Paper Corp. Landfill

**Waste Type**: Paper Mill Sludge

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y** **N**
- Are any trends seen in the COD data? ________________________ **Y** **N**
- Without COD, would the contamination have been discovered?

| | | | | |
|---|---|---|---|---|
| Ammonia N: | Increases | Decreases | Overall Impact | No Data |
| Alkaliinity: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Nitrate + Nitrite: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | | |
|---|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data | |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | *Confusing* |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Cadmium: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| COD: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Iron: | Increases | Decreases | Overall Impact | No Data | |
| Lead: | Increases | Decreases | Overall Impact | No Data | |
| Manganese: | Increases | Decreases | Overall Impact | No Data | |
| Mercury: | Increases | Decreases | Overall Impact | No Data | |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data | |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data | |
| Sodium: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| TSS: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for <u>leachate</u> data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

No VOCs; very high levels for all parameters;
Very similar patterns/trends for most parameters

## Site Name: Marathon County Landfill

**Waste Type**: Municipal Solid Waste

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y** **N**
- Are any trends seen in the COD data? ____________________ **Y** **N**
- Without COD, would the contamination have been discovered?

| | | | | | |
|---|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | *all below PAL* |
| COD: | Increases | Decreases | Overall Impact | No Data | *not helpful* |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | | |
|---|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data | |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | *Hard to tell* |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Cadmium: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | *very high levels* |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Iron: | Increases | Decreases | Overall Impact | No Data | |
| Lead: | Increases | Decreases | Overall Impact | No Data | |
| Manganese: | Increases | Decreases | Overall Impact | No Data | |
| Mercury: | Increases | Decreases | Overall Impact | No Data | |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data | |
| Sodium: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| TSS: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for leachate data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

Lots of VOCs downgradient and in leachate

## Site Name: City of New Richmond Landfill (2492)

**Waste Type**: Municipal Solid Waste

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y** **N**
- Are any trends seen in the COD data? ______MW #1 clear increase_______ **Y** **N**

- Without COD, would the contamination have been discovered?

| | | | | | |
|---|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | *hard to tell* |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | |
|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Cadmium: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Iron: | Increases | Decreases | Overall Impact | No Data |
| Lead: | Increases | Decreases | Overall Impact | No Data |
| Manganese: | Increases | Decreases | Overall Impact | No Data |
| Mercury: | Increases | Decreases | Overall Impact | No Data |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data |
| Sodium: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |
| TSS: | Increases | Decreases | Overall Impact | No Data |

No leachate data at this site

- Are the trends similar among all the parameters for leachate data? **Y** **N**

- Would COD be essential in determining contamination at this site? **Y** **N**

## Site Name: City of Madison - Sycamore Landfill (1935)

**Waste Type**: Municipal Solid Waste

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y** **N**
- Are any trends seen in the COD data? ____________________ **Y** **N**
- Without COD, would the contamination have been discovered?

| | | | | | |
|---|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | *Not Helpful* |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | *Not great* |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | *Not helpful* |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | |
|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Cadmium: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Iron: | Increases | Decreases | Overall Impact | No Data |
| Lead: | Increases | Decreases | Overall Impact | No Data |
| Manganese: | Increases | Decreases | Overall Impact | No Data |
| Mercury: | Increases | Decreases | Overall Impact | No Data |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data |
| Sodium: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |
| TSS: | Increases | Decreases | Overall Impact | No Data |

No leachate data

- Are the trends similar among all the parameters for <u>leachate</u> data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

VOC data lacking and inorganic parameters not convincing

## Site Name:  City of Oconto Falls Landfill

**Waste Type**:  Municipal Solid Waste

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y** **N**
- Are any trends seen in the COD data? ____________________ **Y** **N**
- Without COD, would the contamination have been discovered?

| | | | | |
|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | | |
|---|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Cadmium: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | *Jumps around* |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Iron: | Increases | Decreases | Overall Impact | No Data | |
| Lead: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| Manganese: | Increases | Decreases | Overall Impact | No Data | *Not enough* |
| Mercury: | Increases | Decreases | Overall Impact | No Data | |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data | |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data | |
| Sodium: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | *Not showing much* |
| TSS: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for leachate data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

Leachate plume visible - Contamination discovered and then site began monitoring - VOC exceedances of ES until 1991 in B-15

## Site Name: Weyerhaeuser Company Landfill

**Waste Type**: Paper Mill Sludge

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y N**
- Are any trends seen in the COD data? _No real trends, small increase **Y N**

- Without COD, would the contamination have been discovered?

| | | | | | |
|---|---|---|---|---|---|
| Ammonia N: | Increases | Decreases | Overall Impact | No Data | *Not Helpful* |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | *Confusing* |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | *Confusing* |
| Nitrate + Nitrite: | Increases | Decreases | Overall Impact | No Data | *Confusing* |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for groundwater? **Y N**

| | | | | | |
|---|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data | |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Cadmium: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Iron: | Increases | Decreases | Overall Impact | No Data | *Not enough data* |
| Lead: | Increases | Decreases | Overall Impact | No Data | |
| Manganese: | Increases | Decreases | Overall Impact | No Data | |
| Mercury: | Increases | Decreases | Overall Impact | No Data | |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data | |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data | |
| Sodium: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | |
| TSS: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for <u>leachate</u> data? **Y N**
- **Would COD be essential in determining contamination at this site? Y N**

# Site Name:  City of Wauwatosa Landfill

**Waste Type**:  Municipal Solid Waste Combustor Residue

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between upgradient and downgradient wells for COD data?
  **Somewhat** **Y** **N**
- Are any trends seen in the COD data? ____________________ **Y** **N**

- Without COD, would the contamination have been discovered?

| | | | | | |
|---|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Boron: | Increases | Decreases | Overall Impact | No Data | |
| Cadmium: | Increases | Decreases | Overall Impact | No Data | *high levels in well 1* |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | *Unconvincing* |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Lead: | Increases | Decreases | Overall Impact | No Data | |
| Selenium: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | *Hiigh background* |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | |
|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Cadmium: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Iron: | Increases | Decreases | Overall Impact | No Data |
| Lead: | Increases | Decreases | Overall Impact | No Data |
| Manganese: | Increases | Decreases | Overall Impact | No Data |
| Mercury: | Increases | Decreases | Overall Impact | No Data |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data |
| Sodium: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |
| TSS: | Increases | Decreases | Overall Impact | No Data |

There are 4 leachate head wells at the site, but no sample results are found on GEMS.

- Are the trends similar among all the parameters for leachate data? **Y** **N**

- **Would COD be essential in determining contamination at this site?** **Y** **N**

Lots of VOC PAL exceedances even at the beginning of monitoring

## Site Name: WEPCO Cedar Sauk Landfill

**Waste Type**: Fly or Bottom Ash

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **NA** **Y** **N**
- Are any trends seen in the COD data? _ **NA** **Y** **N**

- Without COD, would the contamination have been discovered?

| | | | | | |
|---|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Boron: | Increases | Decreases | Overall Impact | No Data | *Very High levels* |
| COD: | Increases | Decreases | Overall Impact | No Data | |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | *Confusing* |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | |
|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Cadmium: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Iron: | Increases | Decreases | Overall Impact | No Dat |
| Lead: | Increases | Decreases | Overall Impact | No Data |
| Manganese: | Increases | Decreases | Overall Impact | No Data |
| Mercury: | Increases | Decreases | Overall Impact | No Data |
| Boron: | Increases | Decreases | Overall Impact | No Data |
| Selenium: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |
| TSS: | Increases | Decreases | Overall Impact | No Data |

No leachate data for this site

- Are the trends similar among all the parameters for leachate data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

No VOC data

## Site Name: Refuse Hideaway Landfill

**Waste Type**: Municipal Solid Waste

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **NA** **Y** **N**
- Are any trends seen in the COD data? _____ **NA** **Y** **N**

Any trend or impacts barely seen because of limited data

- Without COD, would the contamination have been discovered?

| | | | | |
|---|---|---|---|---|
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | |
|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Cadmium: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Iron: | Increases | Decreases | Overall Impact | No Data |
| Lead: | Increases | Decreases | Overall Impact | No Data |
| Manganese: | Increases | Decreases | Overall Impact | No Data |
| Mercury: | Increases | Decreases | Overall Impact | No Data |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data |
| Sodium: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |
| TSS: | Increases | Decreases | Overall Impact | No Data |

- Are the trends similar among all the parameters for <u>leachate</u> data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

Need VOC data to detect contamination

## Site Name: Wausau Papers Landfill

**Waste Type**: Paper Mill Sludge

Is COD Useful? Was COD used to determine whether contamination had occurred?

- Was there an overall impact seen between up-gradient and down-gradient wells for COD data? **Y** **N**
- Are any trends seen in the COD data? ________________________ **Y** **N**
- Without COD, would the contamination have been discovered?

| | | | | |
|---|---|---|---|---|
| Ammonia N: | Increases | Decreases | Overall Impact | No Data |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data |
| Chloride: | Increases | Decreases | Overall Impact | No Data |
| COD: | Increases | Decreases | Overall Impact | No Data |
| Conductivity: | Increases | Decreases | Overall Impact | No Data |
| pH: | Increases | Decreases | Overall Impact | No Data |
| Hardness: | Increases | Decreases | Overall Impact | No Data |
| Nitrate + Nitrite: | Increases | Decreases | Overall Impact | No Data |
| Sulfate: | Increases | Decreases | Overall Impact | No Data |

- Are the trends similar among all the parameters for groundwater? **Y** **N**

| | | | | | |
|---|---|---|---|---|---|
| BOD: | Increases | Decreases | Overall Impact | No Data | |
| Conductivity: | Increases | Decreases | Overall Impact | No Data | |
| pH: | Increases | Decreases | Overall Impact | No Data | |
| Alkalinity: | Increases | Decreases | Overall Impact | No Data | |
| Cadmium: | Increases | Decreases | Overall Impact | No Data | |
| Chloride: | Increases | Decreases | Overall Impact | No Data | |
| COD: | Increases | Decreases | Overall Impact | No Data | |
| Hardness: | Increases | Decreases | Overall Impact | No Data | |
| Iron: | Increases | Decreases | Overall Impact | No Data | |
| Lead: | Increases | Decreases | Overall Impact | No Data | |
| Manganese: | Increases | Decreases | Overall Impact | No Data | *slight increase* |
| Mercury: | Increases | Decreases | Overall Impact | No Data | *one outlier* |
| Ammonia N: | Increases | Decreases | Overall Impact | No Data | *data all over* |
| Total Kjeldahl N: | Increases | Decreases | Overall Impact | No Data | *depends on well* |
| Sodium: | Increases | Decreases | Overall Impact | No Data | |
| Sulfate: | Increases | Decreases | Overall Impact | No Data | |
| TSS: | Increases | Decreases | Overall Impact | No Data | *some high points* |

- Are the trends similar among all the parameters for <u>leachate</u> data? **Y** **N**
- **Would COD be essential in determining contamination at this site?** **Y** **N**

COD should be kept because COD had similar graphs to alkalinity and hardness. Also, sulfate and chloride didn't show up in the same wells for groundwater monitoring, conductivity data quite variable, and leachate inconsistent

## Appendix 3: Conductivity Boxplots Using Concentration Values And Non-Parametric Values For Three Landfills

## Oconto Falls Landfill

Figure A3 - 1: Conductivity Box plots using concentration - City of Oconto Falls Landfill, License Number 409

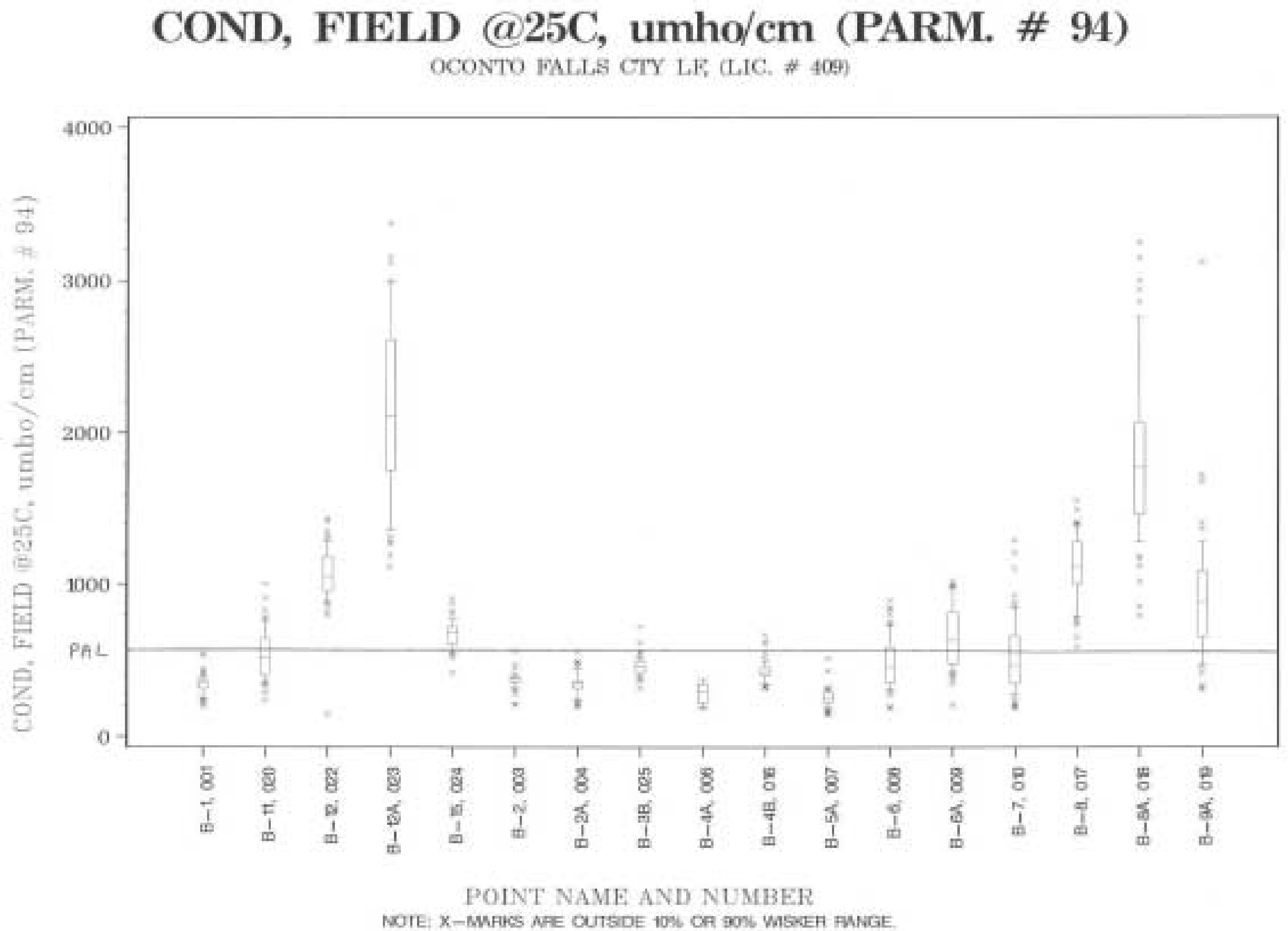
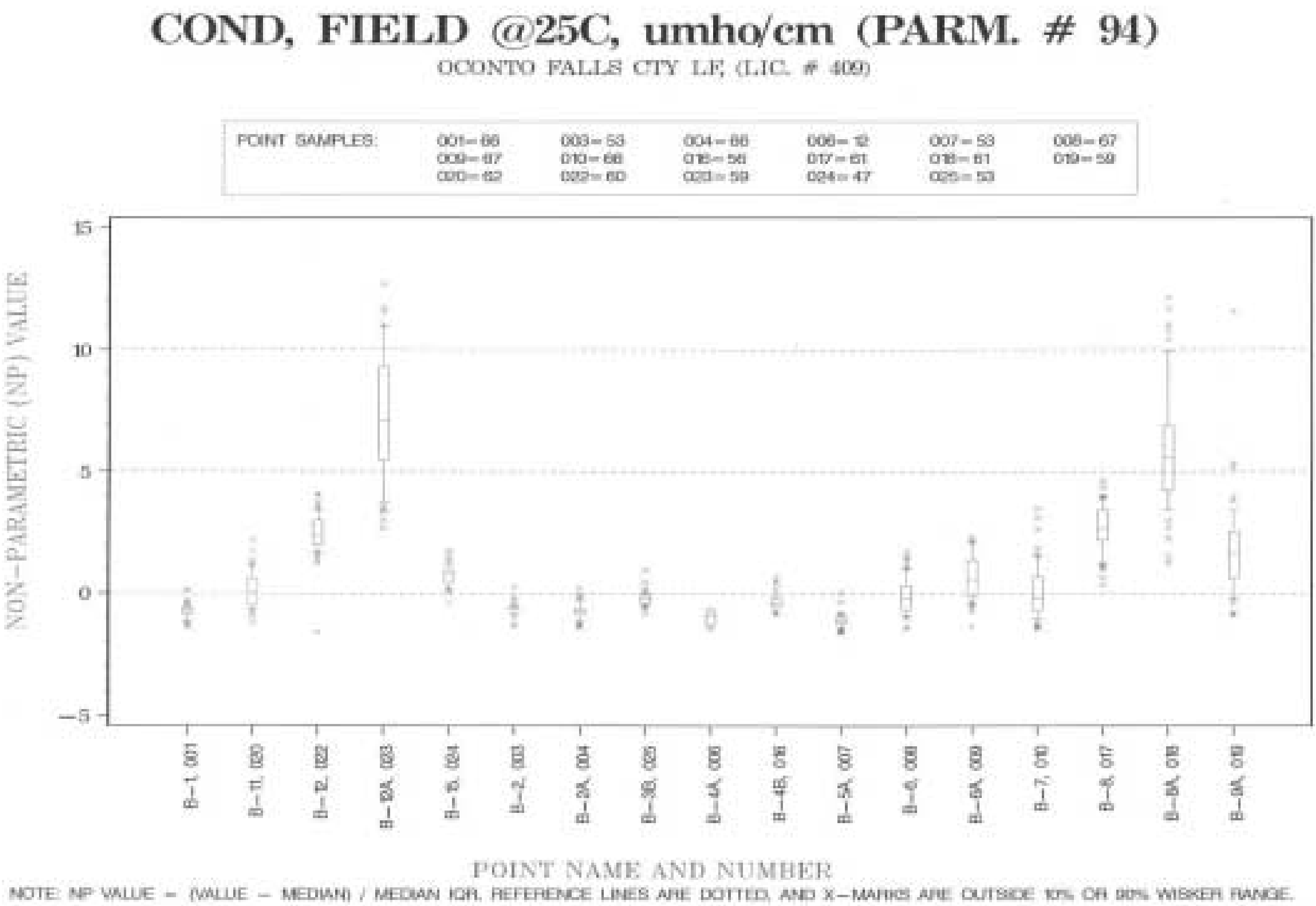


Figure A3 - 2: Conductivity Box plots using non-parametric values - City of Oconto Falls Landfill, License Number 409



## Juneau County Landfill

Figure A3 - 3: Conductivity Box plots using concentration - Juneau County Landfill, License Number 2565

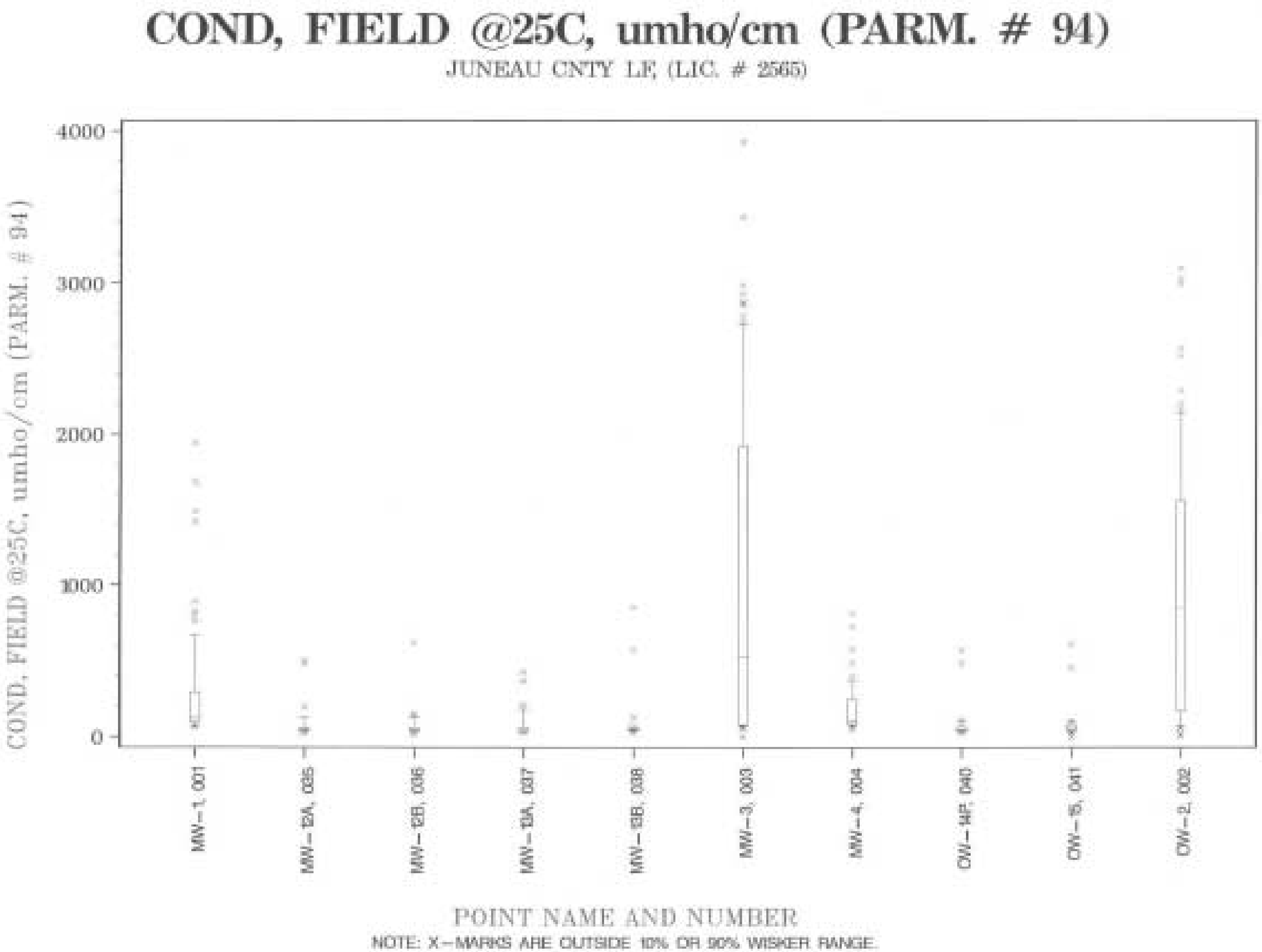
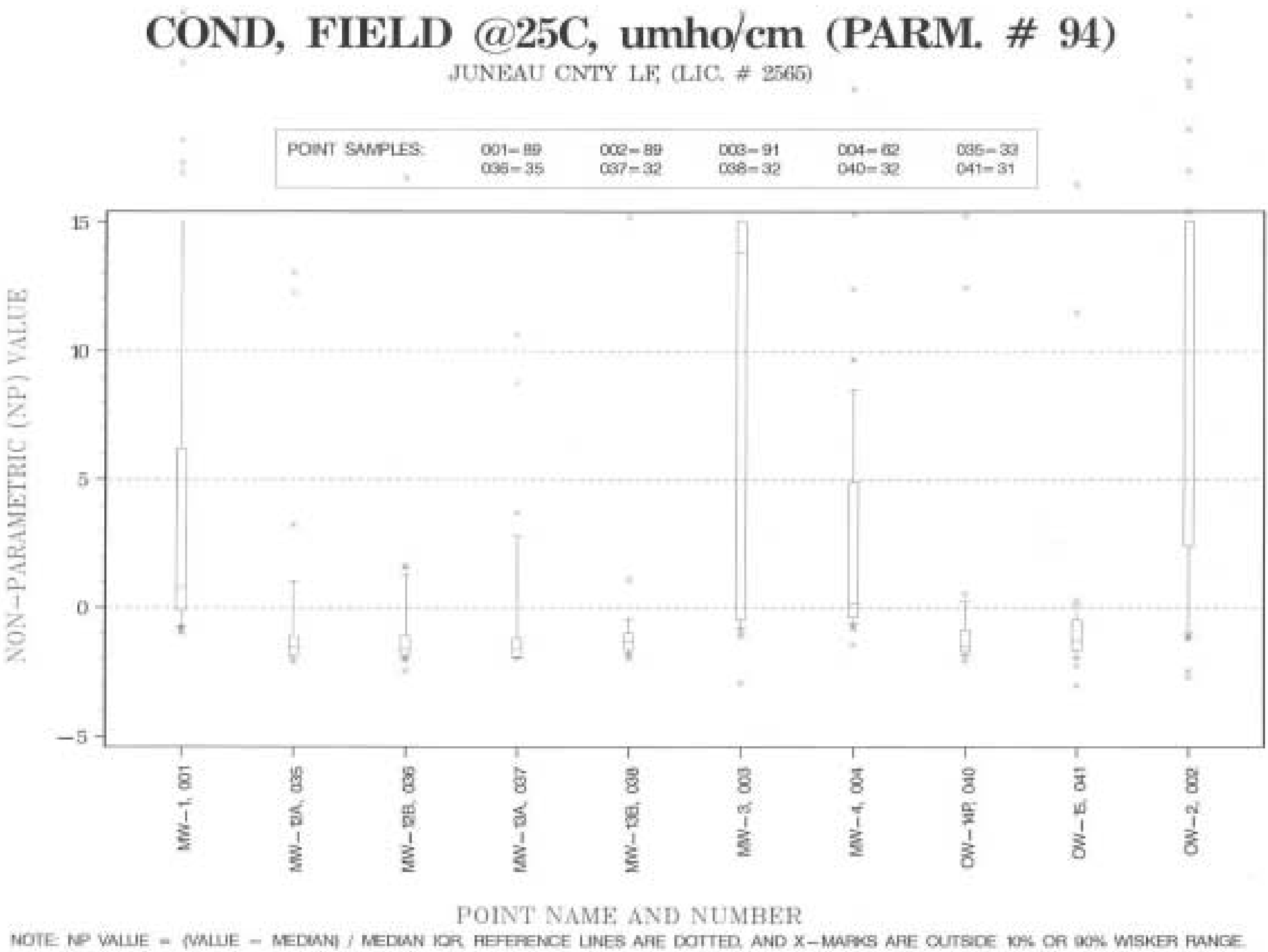


Figure A3 - 4: Conductivity Box plots using non-parametric values -Juneau County Landfill, License Number 2565



## City of New Richmond Landfill

Figure A3 - 5: Conductivity Box plots using concentration - City of New Richmond Landfill, License Number 2492

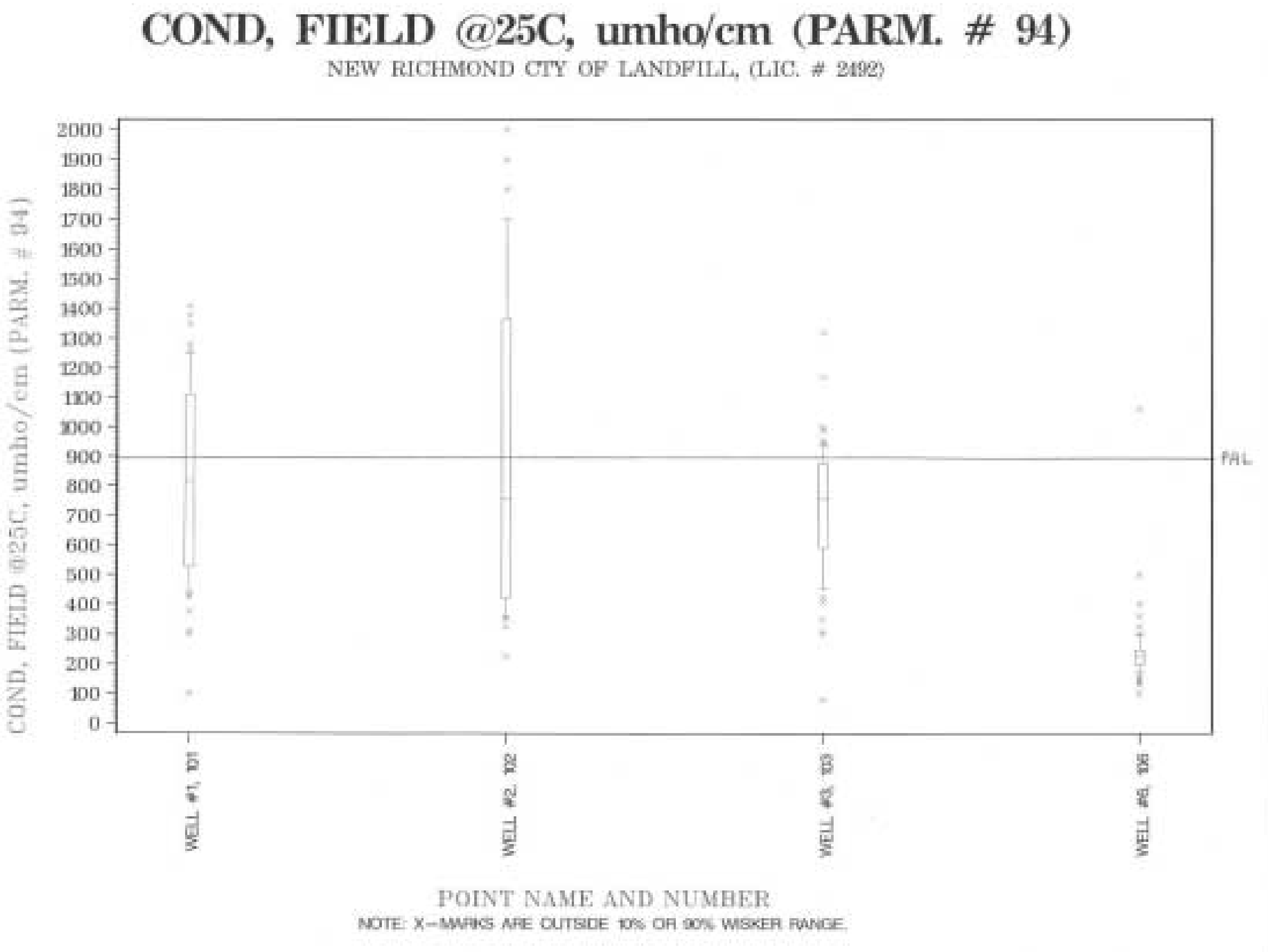
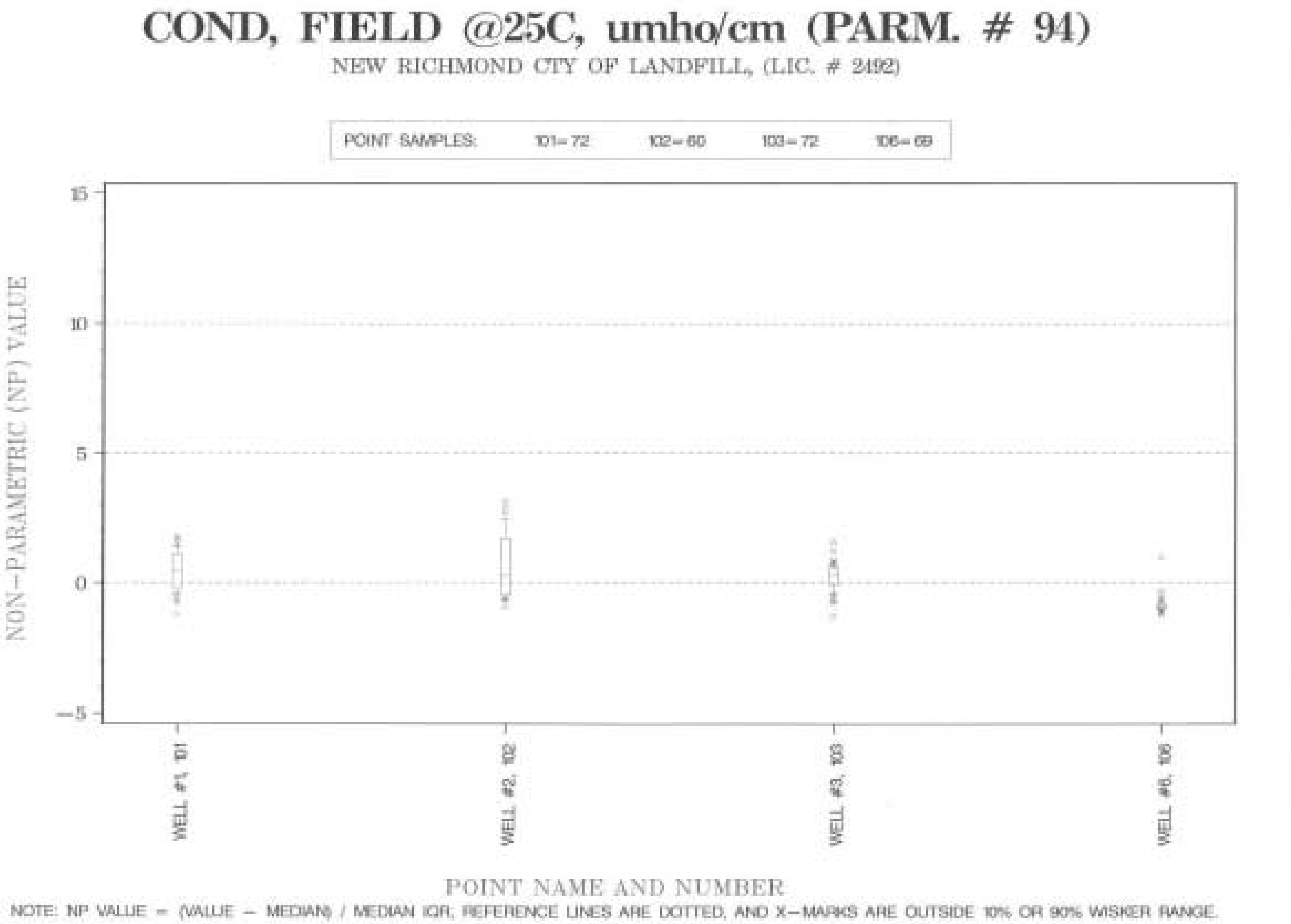


Figure A3 - 6: Conductivity Box plots using non-parametric values - City of New Richmond Landfill, License Number 2492



# Appendix 4: ICP Scan

**ICP metal scan on landfill monitoring well samples collected in Fall, 2000. Concentrations are mg/L.**

| Landfill Name | Well ID | Date | As | Ca | Cu | Fe | K | Mg | Mn | Na | Pb | $SO_4$ | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Amery | MW1 | 09/18/00 | <0.005 | 36.4 | 0.002 | 0.188 | 1.5 | 15.4 | 1.440 | 11.3 | <0.002 | 1451.0 | 0.010 |
| Amery | B1 | 09/18/00 | <0.005 | 15.9 | 0.002 | 0.015 | 0.9 | 5.3 | 0.231 | 2.1 | <0.002 | | <0.001 |
| Amery | MW2 AR | 09/18/00 | <0.005 | 229.3 | 0.002 | 0.015 | 3.9 | 102.7 | 0.084 | 160.5 | <0.002 | | <0.001 |
| Amery | D1 | 09/18/00 | <0.005 | 5.6 | 0.001 | 0.015 | <0.3 | 1.8 | 0.006 | 1.9 | <0.002 | | 0.003 |
| Amery | G2 | 09/18/00 | <0.005 | 21.4 | 0.005 | 0.113 | 1.0 | 8.1 | 0.271 | 2.9 | <0.002 | | <0.001 |
| Amery | B2 | 09/18/00 | <0.005 | 115.7 | 0.003 | 0.038 | 2.0 | 45.5 | 0.190 | 27.9 | 0.002 | | <0.001 |
| Chase | MW1 | 10/24/00 | <0.005 | 97.0 | <0.001 | 0.312 | 3.7 | 94 | 0.235 | 46.4 | 0.002 | 119.1 | 0.004 |
| Chase | MW2 | 10/24/00 | <0.005 | 67.8 | <0.001 | 0.212 | 2.5 | 69.6 | 0.083 | 33.5 | 0.003 | 58.7 | 0.001 |
| Chase | MW3 | 10/24/00 | <0.005 | 77.8 | <0.001 | 0.021 | 1.0 | 38.5 | 0.001 | 6.8 | <0.002 | 14.7 | 0.003 |
| Chase | MW5A | 10/24/00 | <0.005 | 16.7 | <0.001 | 0.045 | 1.0 | 14.5 | 0.043 | 20 | <0.002 | 11.9 | <0.001 |
| Chase | MW5 | 10/24/00 | <0.005 | 101.4 | <0.001 | 2.794 | 5.0 | 80.3 | 0.239 | 42.5 | <0.002 | 113.3 | 0.001 |
| CPI Port | B1R | 10/02/00 | <0.005 | 6.2 | 0.001 | 0.110 | 3.0 | 3.4 | 0.112 | 4.2 | <0.002 | | 0.004 |
| CPI Port | B30 | 10/02/00 | <0.005 | 23.9 | <0.001 | 3.325 | 1.9 | 14.1 | 0.105 | 8.8 | <0.002 | 12.0 | 0.010 |
| CPI Port | B27R | 10/02/00 | <0.005 | 126.1 | <0.001 | 87.612 | 11.0 | 55.1 | 1.831 | 24.3 | 0.015 | | 0.023 |
| CPI Port | B21R | 10/02/00 | <0.005 | 78.0 | <0.001 | 58.339 | 7.1 | 46.7 | 3.219 | 22.9 | 0.012 | 19.1 | 0.019 |
| CPI Port | B26R | 10/02/00 | 0.005 | 81.1 | <0.001 | 114.328 | 9.8 | 19 | 2.432 | 3.5 | 0.021 | | 0.020 |
| CPI Wood | MW 31 | 10/09/00 | <0.005 | 6.1 | 0.004 | 9.093 | 0.7 | 1.8 | 0.091 | 3.1 | <0.002 | | 0.003 |
| CPI Wood | MW 14 | 10/09/00 | <0.005 | 15.5 | 0.036 | 3.000 | 4.3 | 5.4 | 0.277 | 10.1 | 0.002 | | 0.011 |
| CPI Wood | MW 14A | 10/09/00 | <0.005 | 46.1 | <0.001 | 22.958 | 2.0 | 14.4 | 0.388 | 19.8 | 0.005 | | 0.002 |
| CPI Wood | MW 9R | 10/09/00 | <0.005 | 26.1 | 0.002 | 3.572 | 16.8 | 12.2 | 0.372 | 26.9 | <0.002 | | 0.012 |
| CPI Wood | MW 8R | 10/09/00 | <0.005 | 85.3 | <0.001 | 30.695 | 23.1 | 48.8 | 0.889 | 47.8 | 0.005 | | 0.004 |
| Frazier | FOW5 | 10/04/00 | <0.005 | 39.2 | <0.001 | 18.200 | 1.2 | 13.6 | 4.115 | 4 | 0.005 | 39.1 | 0.004 |
| GP | ST 15 | 09/05/00 | <0.005 | 117.9 | 0.007 | 0.044 | 6.0 | 41.2 | 0.562 | 141.5 | <0.002 | 279.4 | 0.019 |
| GP | 44 AR | 09/05/00 | <0.005 | 258.1 | <0.001 | 28.739 | 84.8 | 70.2 | 2.474 | 93.9 | 0.007 | 163.7 | 0.011 |
| GP | 82 WT | 09/05/00 | <0.005 | 2.8 | <0.001 | 0.026 | 0.7 | 0.8 | 0.003 | 2.8 | <0.002 | 7.1 | 0.004 |
| GP | 85 WT | 09/05/00 | <0.005 | 62.6 | 0.002 | 0.026 | 2.0 | 25.4 | 0.006 | 15.2 | <0.002 | 134.2 | 0.004 |
| GP | 85 PS | 09/05/00 | <0.005 | 177.6 | 0.002 | 0.016 | 2.4 | 88.1 | 0.197 | 20.8 | 0.002 | 330.2 | 0.004 |
| Juneau | MW2 | 09/21/00 | <0.005 | 43.4 | <0.001 | 53.829 | 57.3 | 42.3 | 0.078 | 56 | 0.01 | 10.2 | 0.033 |
| Juneau | MW14A | 09/21/00 | <0.005 | 3.1 | 0.005 | 0.014 | 1.5 | 1.3 | 0.008 | 0.6 | <0.002 | 11.1 | 0.022 |
| Juneau | OW1 | 09/21/00 | <0.005 | 43.0 | <0.001 | 62.958 | 13.9 | 20.6 | 6.171 | 6.9 | 0.012 | | 0.353 |
| Juneau | DSMW3 | 09/21/00 | <0.005 | 7.6 | 0.001 | 0.011 | 2.0 | 3.5 | 0.001 | 2.2 | <0.002 | 20.4 | 0.003 |
| Juneau | 14B | 09/21/00 | <0.005 | 3.0 | <0.001 | 0.008 | 1.3 | 0.9 | 0.003 | 1 | <0.002 | | 0.002 |
| Marathon | R-13 | 09/08/00 | <0.005 | 115.8 | 0.001 | 3.371 | 1.3 | 69.1 | 0.463 | 5 | 0.003 | 10.8 | 0.006 |
| Marathon | R-30 | 09/08/00 | <0.005 | 41.1 | 0.006 | 0.868 | 1.4 | 26.2 | 0.030 | 6.1 | <0.002 | 17.8 | 0.023 |
| Marathon | R-37 | 09/08/00 | <0.005 | 41.7 | 0.005 | 0.049 | 1.0 | 21.9 | 0.003 | 2.6 | <0.002 | 15.5 | 0.021 |
| Marathon | R-38A | 09/08/00 | <0.005 | 75.4 | <0.001 | 0.047 | 1.1 | 37.7 | 0.170 | 4.5 | <0.002 | 8.9 | 0.004 |
| Marathon | R-40 | 09/08/00 | <0.005 | 51.1 | <0.001 | 0.012 | 0.9 | 25.9 | 0.007 | 2.4 | <0.002 | 11.0 | 0.001 |
| Marinette | MW1 | 09/06/00 | 0.037 | 147.1 | <0.001 | 1.289 | 142.3 | 127.8 | 0.047 | 266.5 | <0.002 | 11.6 | 0.170 |
| Marinette | MW2 | 09/06/00 | <0.005 | 46.8 | <0.001 | 3.961 | 1.0 | 15.2 | 0.096 | 1.8 | <0.002 | 13.7 | 0.696 |
| Marinette | MW3 | 09/06/00 | <0.005 | 22.8 | <0.001 | 16.189 | 0.9 | 13 | 0.160 | 1.5 | 0.004 | 10.2 | 0.226 |
| Mineral Pt | 5A | 09/14/00 | <0.005 | 124.4 | 0.003 | 0.014 | 7.1 | 65.8 | 0.011 | 56.3 | <0.002 | 32.8 | 0.002 |
| Mineral Pt | 5B | 09/14/00 | <0.005 | 101.0 | <0.001 | 0.005 | 4.2 | 53.2 | <0.001 | 67.6 | <0.002 | 25.6 | <0.001 |
| Mineral Pt | 10A | 09/14/00 | <0.005 | 91.4 | <0.001 | 0.084 | 3.1 | 45.8 | 0.005 | 79.8 | <0.002 | 20.4 | 0.001 |
| Mineral Pt | 10B | 09/14/00 | <0.005 | 93.4 | <0.001 | -0.002 | 2.8 | 47.7 | <0.001 | 84.6 | <0.002 | 21.2 | <0.001 |
| Mineral Pt | 11A | 09/14/00 | <0.005 | 80.8 | 0.001 | 0.024 | 2.8 | 41.4 | 0.001 | 82.6 | <0.002 | 16.2 | 0.003 |
| New Richm | MW1 | 09/20/00 | <0.005 | 54.4 | <0.001 | 11.127 | 2.3 | 106.6 | 0.842 | 36.3 | <0.002 | | 0.004 |
| New Richm | MW3 | 09/20/00 | <0.005 | 114.6 | 0.001 | 0.010 | 4.8 | 52.5 | 0.001 | 18.3 | <0.002 | 30.1 | 0.004 |
| New Richm | MW6 | 09/20/00 | <0.005 | 23.4 | <0.001 | 0.007 | 1.3 | 11.1 | <0.001 | 2.6 | <0.002 | 7.4 | <0.001 |
| New Richm | MW2 | 09/20/00 | <0.005 | 180.6 | 0.001 | 0.004 | 3.0 | 122.2 | 0.005 | 198.5 | 0.003 | 240.7 | 0.003 |

| Landfill Name | Well ID | Date | As | Ca | Cu | Fe | K | Mg | Mn | Na | Pb | $SO_4$ | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oconto | B6 | 09/25/00 | 0.008 | 87.6 | <0.001 | 6.536 | 1.6 | 26.9 | 0.307 | 3 | 0.002 | | 0.007 |
| Oconto | B6A | 09/25/00 | 0.009 | 119.7 | <0.001 | 9.637 | 1.6 | 41.4 | 0.281 | 2.1 | 0.002 | | 0.003 |
| Oconto | B7 | 09/25/00 | <0.005 | 85.6 | <0.001 | 3.394 | 1.5 | 43.6 | 0.550 | 2.3 | <0.002 | 5.1 | <0.001 |
| Oconto | B8 | 09/25/00 | 0.007 | 120.4 | <0.001 | 17.472 | 8.7 | 43.4 | 0.503 | 18.5 | 0.003 | | 0.007 |
| Oconto | B8A | 09/25/00 | <0.005 | 201.4 | <0.001 | 17.374 | 6.3 | 48.8 | 0.462 | 4.5 | 0.003 | | 0.006 |
| Oconto | B12 | 09/25/00 | <0.005 | 115.5 | <0.001 | 17.380 | 12.5 | 39.3 | 0.483 | 18.7 | 0.004 | | 0.013 |
| Oconto | B12A | 09/25/00 | 0.008 | 249.7 | 0.001 | 32.086 | 62.6 | 91.4 | 2.465 | 74.1 | 0.018 | | 0.019 |
| Plainwell | 17 | 09/19/00 | <0.005 | 73.5 | <0.001 | 77.135 | 1.8 | 19.6 | 2.984 | 8.3 | 0.014 | | 0.011 |
| Plainwell | 9 | 09/19/00 | 0.007 | 47.3 | 0.002 | 23.470 | 3.2 | 12.2 | 1.011 | 38 | 0.004 | 6.1 | 0.084 |
| Plainwell | P(18) | 09/19/00 | <0.005 | 12.4 | <0.001 | 0.011 | 2.2 | 4.8 | 0.001 | 2.4 | 0.002 | 15.1 | 0.005 |
| Plainwell | 9A | 09/19/00 | 0.021 | 49.7 | <0.001 | 46.069 | 1.4 | 16.4 | 1.751 | 33.5 | 0.008 | 10.8 | 0.014 |
| Plainwell | 17A | 09/19/00 | <0.005 | 42.4 | <0.001 | 46.146 | 3.0 | 12.3 | 2.140 | 12.6 | 0.009 | 11.2 | 0.015 |
| Portage | MW12 | 08/31/00 | <0.005 | 56.8 | <0.001 | 0.006 | 1.4 | 28.6 | <0.001 | 3.3 | <0.002 | 8.7 | 0.014 |
| Portage | 20P | 08/31/00 | <0.005 | 59.4 | <0.001 | 0.009 | 1.3 | 30.4 | <0.001 | 2.1 | <0.002 | 8.9 | <0.001 |
| Portage | MW21 | 08/31/00 | <0.005 | 74.3 | <0.001 | 0.014 | 1.4 | 38.1 | <0.001 | 2.1 | <0.002 | 9.7 | <0.001 |
| Portage | MW23 | 08/31/00 | <0.005 | 121.9 | <0.001 | 0.024 | 1.6 | 60.6 | 0.002 | 4.2 | <0.002 | 9.9 | 0.002 |
| Portage | 23P | 08/31/00 | <0.005 | 58.1 | <0.001 | 0.010 | 1.2 | 29.1 | <0.001 | 2.2 | <0.002 | 9.1 | <0.001 |
| Pound | UGW1 | 10/24/00 | <0.005 | 78.7 | <0.001 | 1.584 | 0.4 | 30.7 | 0.110 | 1.9 | <0.002 | 6.2 | 0.004 |
| Pound | SGW3 | 10/24/00 | <0.005 | 67.2 | 0.002 | 0.114 | 0.6 | 24.7 | 0.062 | 2.2 | <0.002 | 8.0 | 0.002 |
| Pound | DGW4 | 10/24/00 | <0.005 | 72.8 | <0.001 | 1.316 | 37.5 | 44.9 | 0.142 | 30.1 | <0.002 | 103.3 | 0.002 |
| Pound | DGW5 | 10/24/00 | <0.005 | 75.8 | <0.001 | 1.805 | 2.4 | 28.6 | 0.096 | 7.2 | <0.002 | 9.6 | 0.001 |
| Pound | SGW6 | 10/24/00 | <0.005 | 64.1 | 0.002 | 0.041 | 0.3 | 23.4 | 0.029 | 1.6 | 0.003 | 13.0 | <0.001 |
| Sycamore | 14A | 09/15/00 | <0.005 | 153.9 | 0.001 | 0.018 | 1.0 | 91.1 | 0.012 | 6.9 | 0.002 | 45.3 | <0.001 |
| Sycamore | 14B | 09/15/00 | <0.005 | 135.1 | 0.001 | 0.008 | 1.4 | 76 | 0.005 | 13.2 | <0.002 | 23.2 | 0.007 |
| Sycamore | 18A | 09/15/00 | <0.005 | 101.3 | 0.001 | 0.047 | 2.7 | 51.2 | 0.024 | 44.8 | <0.002 | 34.2 | 0.001 |
| Sycamore | 18B | 09/15/00 | <0.005 | 95.2 | 0.002 | 0.013 | 3.1 | 51.7 | 0.004 | 47.3 | <0.002 | 34.5 | 0.004 |
| Sycamore | 23A | 09/15/00 | <0.005 | 92.6 | 0.001 | 0.005 | 3.6 | 50.1 | 0.002 | 17.6 | <0.002 | 28.9 | <0.001 |
| Wausau | P8 | 09/12/00 | <0.005 | 22.9 | 0.007 | 0.049 | 1.4 | 22 | 0.063 | 5 | <0.002 | 20.5 | 0.058 |
| Wausau | P11 | 09/12/00 | <0.005 | 10.2 | 0.005 | 0.069 | 1.2 | 3.9 | 2.017 | 5.1 | <0.002 | 5.4 | 0.046 |
| Wausau | P17 | 09/12/00 | <0.005 | 15.8 | 0.003 | 0.114 | 1.1 | 5.4 | 0.020 | 7.4 | <0.002 | 17.5 | 0.044 |
| Wausau | P23 | 09/12/00 | 0.005 | 27.7 | 0.001 | 19.525 | 55.0 | 253.6 | 2.844 | 15.7 | 0.004 | 11.4 | 0.087 |
| Wausau | P27 | 09/12/00 | <0.005 | 23.3 | 0.002 | 3.717 | 1.3 | 6.7 | 3.626 | 3.3 | <0.002 | 14.8 | 0.040 |
| Weston | MW7 | 09/07/00 | <0.005 | 29.2 | 0.023 | 15.937 | 16.9 | 5.8 | 3.452 | 30.5 | 0.006 | 13.0 | 0.066 |
| Weston | MW8 | 09/07/00 | <0.005 | 27.4 | 0.001 | 0.970 | 2.7 | 8.3 | 18.491 | 15.4 | 0.003 | 45.6 | 0.016 |
| Weston | MW8P | 09/07/00 | <0.005 | 43.2 | 0.003 | 2.156 | 5.3 | 11 | 1.385 | 12.8 | 0.003 | 13.8 | 0.020 |
| Weston | MW9P | 09/07/00 | <0.005 | 27.2 | <0.001 | 0.048 | 1.4 | 11.6 | 0.012 | 19.7 | 0.003 | 9.6 | 0.013 |
| Weston | MW14P | 09/07/00 | <0.005 | 19.2 | 0.007 | 0.019 | 2.3 | 6.3 | 0.016 | 19.3 | <0.002 | 8.6 | 0.036 |